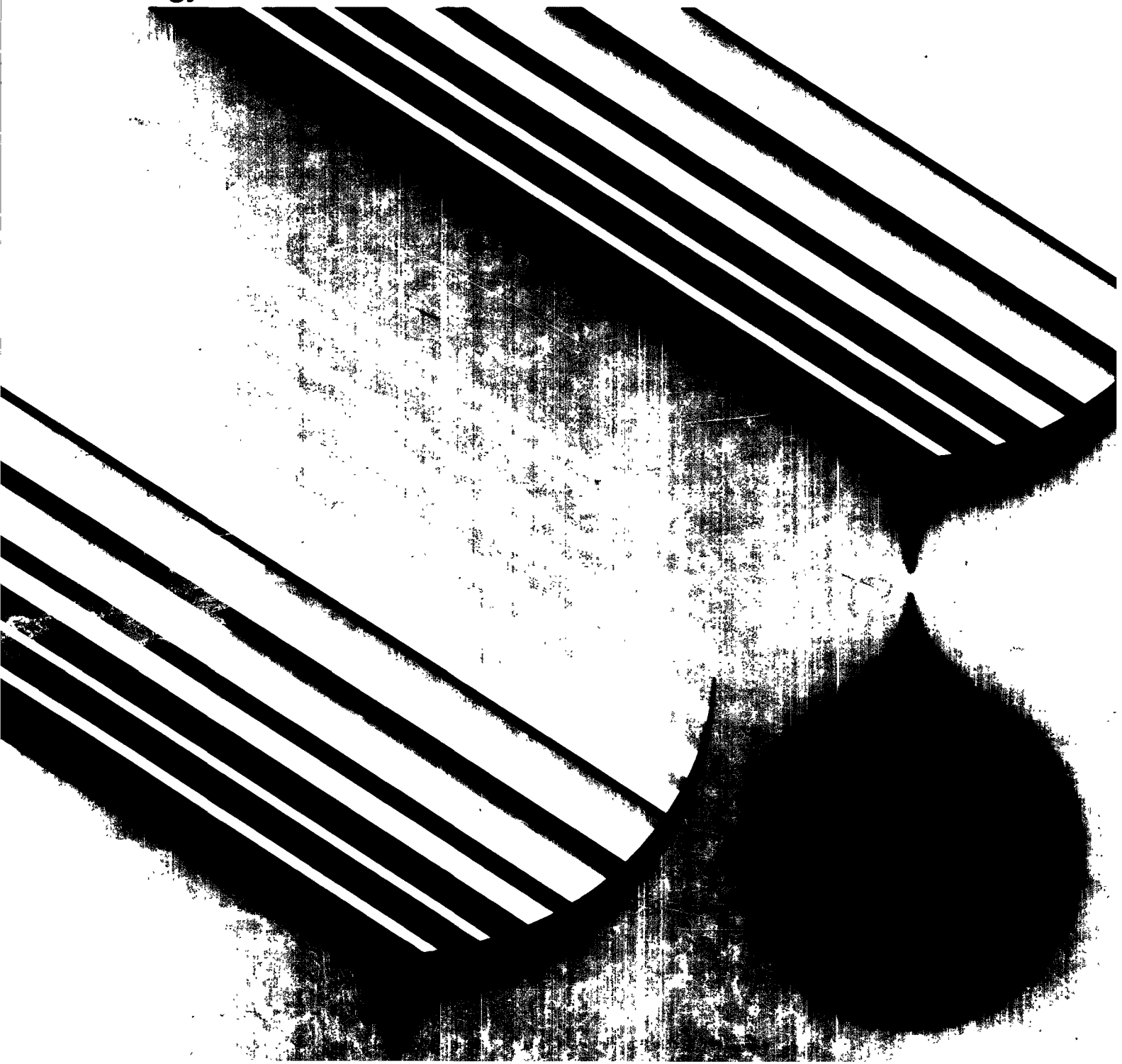# Waste Treatment

Upgrading Metal-Finishing Facilities to Reduce Pollution

EPA Technology Transfer Seminar Publication

WASTE TREATMENT

Upgrading Metal-Finishing Facilities
to Reduce Pollution

ENVIRONMENTAL PROTECTION AGENCY ● Technology Transfer

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INTRODUCTION

THE NEED FOR WASTE TREATMENT

Metal processing in manufacturing includes a number of finishing steps that improve and condition the surface for further processing for the intended final purpose of an article. Most of these finishing steps employ wet processes and require rinsing steps. Water pollution is caused by the deliberate or accidental discharge of the processing solutions and the contaminated rinse water. The process may be directed toward:

- Cleaning, which is the removal of surface oils, greases, buffing compounds, and the like

- Removal of oxides, rust, scale, and other materials

- Electrochemical or chemical processing to provide the basis metal with a surface coating consisting of a plated metal or a chemically deposited, so-called conversion coating such as phosphate and oxide film as in blackening

The general aims are to change the surface of a product to:

- Improve corrosion resistance

- Make the appearance more pleasing

- Improve hardness

- Increase wear resistance

- Change surface conductivity

- Finish to suit specific engineering applications.

It is evident that the first steps in the process—cleaning and oxide removal—are mainly preparatory steps for good adhesion and receptivity for the subsequent finishes to be employed. These preparatory steps may be similar to the procedures used in the primary metal-manufacturing industries or by the manufacturers of certain finished products (such as automobiles and appliances). They are, however, a major part of the activity in an electroplating plant, while they are steps of relatively minor importance for the manufacturer.

An electroplating plant may also be engaged in mechanical finishing activities, such as polishing and buffing, sandblasting, or wire brushing. It may have cleaning or painting processes employing solvents, mainly various chemical solutions using water as a solvent for the chemicals and as a rinsing medium between the various process solutions through which the work progresses.

In an activity centered around various processes employing water as a solvent, it is evident that water-pollution problems will be encountered whenever an effluent is discharged. The severity of the pollution naturally will depend on the source of waste, the type of process employed, the size of the installation, the relative concentration of the effluent, and so forth.

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ENGINEERING CONSIDERATIONS

Waste-treatment processes aim to eliminate from the effluent stream the polluting ingredients. An engineering function selects and coordinates the various treatment steps, decides the required size of equipment, selects the best site to meet plant requirements, and provides the necessary plans, specifications, and operating information, aiming for a treatment plant that, when properly operated, will insure that the effluent will meet the design criteria. The engineer who designs such a plant must have information from many sources to be able to meet his objectives.

Each plant uses a finishing program unique to itself. The processes used and the makeup of processing solutions are highly variable. The processing equipment employed will differ in individual features, drainage rates, foundation, floor contours, age—all factors to be considered. The production volume, type, and shape of the articles will determine the surface area to be processed and the anticipated dragout rates per unit of surface area. The various finishing processes contain a variety of contaminants; these must be known to judge the type of material to be removed from the waste stream. The applicable chemical processes must be selected to insure the desired reactions.

Because the economy of the manufacturing process is affected, the treatment plant and its anticipated operating costs are of paramount importance. Process solution regeneration, chemical and metals recovery, water reuse and water savings, and operating and supervisory labor costs are all factors to be considered.

The flow rate in the receiving stream, the capacity of the municipal sewage-treatment plant, and the applicable Federal, State, and local requirements will have great bearing on the formulation of design criteria for the effluent to be discharged. Plant safety, Occupational Safety and Health Act (OSHA) regulations, and specific local requirements—for example, the Pennsylvania Pollution Incident Prevention Plan—must be considered.

SOURCES OF WASTE

Dumping of Waste Process Solutions

The cleaning- and descaling-process solutions are so formulated that they will remove soil or scale and surface metal film, and will hold the removed material without depositing it back on the work being processed. Naturally, the capacity for additional soil or metal removal will slowly be reduced as the soil or metal content of the cleaning solution rises, until finally the particular cleaning solution is considered spent and is dumped. The dumping can occur as a batch waste discharge, or perhaps as a continuous, slow wastage to maintain a certain uniform concentration of active cleaning compounds or acids with a uniform contaminant loading or metal concentration to avoid the necessity of batch dumping.

Batch discharges occur periodically. The relative volume of waste is usually not large; but as the chemical concentration is relatively high, the pollution effect may be considered relatively serious.

The cleaners employed in metal finishing usually are compounded with various alkali phosphates and relatively high concentrations of wetting agents to provide fast and complete oil, grease, and soil removal. The various acid solvents for metal removal may contain higher concentrations than normal in the primary manufacturing industry because of the greater demands for utmost cleanliness of the metal film for subsequent processing and because the usual demands for bright finishes require high concentrations of acid solutions and frequent dumping to maintain a low metal contaminant level in the acid cleaners in use.

Most of the electrochemical process solutions in use—such as electroplating and anodic treatment solutions—can be maintained in working order by periodic or continuous filtration, purification, or additions of various chemicals. But many process solutions employed in finishing either cannot be completely purified or are uneconomical to purify, in which case the process solution itself will reach a point where dumping is necessary and a new process solution must be made up. This category would include, for example, chromium plating solutions contaminated by iron, copper, nickel, etc., anodizing solutions for aluminum processing, some of the cyanide-type plating solutions, and chromating- or phosphating-type conversion-coating processes.

From a pollution-hazard standpoint, these wasted process solutions may be considered primary subjects for waste treatment. In view of the periodic or infrequent discharges, the relatively small volume, and ample time available for proper treatment, the waste-treatment effort is relatively small. Because of the high concentrations of chemicals to be discharged, the pollution effect can be most severe. It will be evident, then, that the chemical consumption for treatment may also be significant. The considerable time available between batch discharges and the usually small total volume to be treated, on the other hand, may allow small-sized equipment to be used.

Accidental Discharges of Process Solutions

The second most severe pollution hazard in connection with metal-finishing operations is from accidental discharges of key process solutions. The concern shown for the treatment of the periodically dumped process waste should be multiplied with regard to the accidental loss of process solutions, because not only is this hazard present for the few process solutions that are assumed to have finite life, but it may affect the contents of processing vats that under normal conditions could be maintained by the usual purification maintenance practiced in the particular plant.

Nearly every process solution in the plant is prone to accidental discharge, mainly because in the past no engineering effort was directed to the avoidance of such discharge. The usual plant layout is such that the entire processing area drains onto the floor, and the floor is only an extension of the sewer system leaving the area.

While it is not common for a plating tank to spring a leak of such magnitude that the entire plating solution could leak away undetected, many plants are operated haphazardly so that a slow leak amounting to a solution loss of 1 to 2 inches per day could go undetected for months. And it is common practice to make up evaporation losses by adding water with a hose to a process solution or by turning on a spigot to the process tank, which may be neglected until the solution overflows the rim.

Filter hoses, heat-exchanger connections, and pumped process lines are all prone to leak. Hoses deteriorate, and so forth. Waste-treatment engineering would anticipate a certain frequency of accidental spillage, depending on the general maintenance in the particular plant.

Steam coils or heat exchangers undergo slow corrosion reactions, and it may be anticipated that pinpoint corrosion or a corrosion cracking will perforate the barrier between the process solution and heat-exchange medium—that is, between solution and steam condensate or water. As the steam condenses, a vacuum forms in the heating coil or in the jacket of the heat exchanger, drawing in the process solution through the voids created by the corrosion action. Proper waste-treatment engineering would therefore concern itself with the accidental contamination of either the steam condensate or the cooling water used in the particular process.

Some State codes require containment of the most toxic process solutions, such as cyanide and chromic acid plating solutions, by a surrounding outer container capable of holding the entire volume of the process solution in case of accident. No doubt these State codes reflect experience accumulated with various plating operations. The fallacy of these regulations is that, as discussed earlier,

there are many other ways for serious accidents to occur and cause severe pollution conditions against which the outer container for the process vat would provide no insurance. The container only protects against the *least* common occurrence—a serious leak in the process tank itself—while adding to the cost of the plant installation.

On the other hand, the awareness of the regulatory agencies of some of the potential hazards with the so-called accidents in a metal-finishing installation should help in a waste-treatment engineering effort aiming for the utmost safety considering the particular plant and processes under scrutiny. The Pennsylvania Pollution Incident Prevention Program regulations require that the engineer submit detailed plans for each installation that stores, uses, or processes toxic or potentially harmful materials. Compliance naturally requires that facilities be incorporated and value judgments be made not only for the processing area, but for lagoons, containment sumps, chemical storage tanks, storage areas, and so forth.

There are also special conditions created by plant locale that may cause accidental pollution; for example, earthquake hazards should be considered in areas such as California, Japan, and Mexico.

Table 1 lists some of the more common accidental discharges, with methods for detection and prevention or correction.

Table 1.—*Common waste discharges due to accidents in metal-finishing plants*

Source	Method of detection	Correction or prevention
1. Process tank overflow a. Unattended water additions. b. Leak of cooling water into solution from heat exchanger or cooling coil.	1. High-level alarms in floor collection system to signal unusual discharges. 2. Integrated floor-spill treatment.	1. Proper floor construction for floor-spill segregation and containment (curbs, trenches, pits). 2. Treatment facilities for collected floor spill. 3. Integrated floor-spill treatment system. 4. Use of spring-loaded valves for water additions. 5. Automatic level controls for water additions.
2. Process solution leakage a. Tank rupture or leakage. b. Pump, hose, pipe rupture or leakage, filtration, heat exchanger, etc. c. Accidental opening of wrong valve.	Same for process tank overflow.	Same as 1-3 for process tank overflow.
3. Normal drippage from workpieces during transfer between process tanks.	Inspection.	1. Drainage pans between process tanks so that drippage returns to the tanks. 2. Floor-spillage collection. 3. Integrated floor-spill treatment.
4. Process solution entering cooling water (heat-exchanger leak).	1. Conductivity cell and bridge to actuate an alarm. 2. Use of the cooling water as rinse water in a process line where the contamination will be immediately evident.	
5. Process solution entering steam condensate (heat exchanger or heating coil leak).	Conductivity cell and bridge to actuate an alarm.	Conductivity controller to switch contaminated condensate to a waste-collection and -treatment system.
6. Spillage of chemicals when making additions to process tanks or spillage in the chemical storage area.	Solution maintenance man responsible for chemical additions.	1. Careful handling and segregation of chemical stores. 2. Segregation and collection of all floor spillage. 3. Integrated floor-spill treatment.

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Contaminated Rinse-Water Effluent

When generally discussing waste treatment in connection with metal-finishing processes, it is normally assumed that the topic will be the elimination of the toxic constituents from the rinse-water effluent. As discussed earlier, the most severe hazards are not from the discharge of an un-treated rinse-water effluent.

Metal finishing requires copious quantities of water to wash away the remaining chemical film on the work surface dragged out from one process solution before the workpiece enters the next process. First, water is the common solvent for this purpose. Second, the removal of the tenaciously adhering chemical film can be more easily accomplished with fast-flowing water, which provides agitation around the work surface. A chemical film dragged out from one process and remaining on the work surface may react with the next process solution to precipitate insoluble salts on the metal surface as barriers for good adhesion, causing subsequent roughness and other defects. The chemicals that may be dragged from one process into the next could cause contamination of the second process solution by the slow accumulation of dragged-in impurities, chemical constituents of the first process. Good rinsing is also needed to eliminate any chemicals remaining in the pores of finished work that may lead to later discoloration, tarnishing, or corrosion, and that this may destroy the desired finish.

The rinse-water effluent from a metal-finishing plant will contain the various dissolved solids which were originally carried on the work surfaces. The dragout from alkali cleaners becomes mixed with the dragout from acids, pickling solutions, and the various plating processes. While the total dissolved salt concentration in the water may not increase significantly, the effluent carries—either as dissolved or as precipitated suspended solids—the various metal salts, cleaning compounds, and anions of the acids used and possibly a small quantity of the oils and greases originally removed by the cleaners from the work surface.

The relatively large volume of effluent discharged makes the treatment of the rinse-water effluent the major problem. It is an additional problem that after all the various process rinses are mixed, the proper chemical treatment becomes much more complicated, or even impossible. In such a case, it may be necessary to segregate the rinse waters into various chemical groupings to pro-vide proper treatment. Mixing of the total effluent occurs only *after* the segregated effluent waste streams have received specific chemical treatment.

PROCESSES REQUIRING POLLUTION CONTROL

There follow some typical metal-finishing processes that require in-plant or waste-treatment control:

- Effluents containing only solid, mechanically produced impurities, such as rolling or annealing scale, sand, or sludge

- Effluents containing liquid impurities that are immiscible with water, such as greases, oils and their solvents including kerosene, benzene, trichlorethylene, and similar solvents

- Effluents from acid pickling solutions for ferrous and nonferrous metals

- Effluents from chemical or electropolishing solutions formulated with mineral acids such as phosphoric, sulfuric, chromic, nitric, and organic acids—such as acetic, citric, gluconic—with high concentration of dissolved metals

- Effluents from phosphating solutions that contain phosphoric acid and metals such as iron, zinc, or manganese

- Effluents from alkaline pickling solutions for aluminum and zinc, including the alkaline cleaners

- Effluents from various types of electroplating solutions, including acid, alkaline, and cyanide solutions from which various metals may be deposited

- Effluents from chromic acid and chromate solutions in the form of electroplating, etching, and anodizing solutions—including chromating solutions for magnesium, zinc, and aluminum—and electropolishing solutions

- Effluents from metal heat treatment, such as cyanide hardening operations, quench waters after brazing, metal and paint stripping, water-wash paint-spray booths, metal etching, typographical and rotogravure operations, and nonelectrolytic plating systems used for metal deposition on nonconductors

Almost all of the chemical-processing solution must be discarded, owing to the buildup of foreign metal impurities. As a general rule, electroplating solutions are seldom, if ever, discarded. When it is necessary to discard spent processing solutions, they are generally batch treated before disposal. The rinse waters following these processing operations usually contain impurities in dilute form. Except in the case of purely mechanical contamination, most of the contamination constituents are highly toxic and these toxic effects usually persist even at low concentrations. Even with large volumes of water it is impossible to dilute the contaminate sufficiently below the toxic levels. For example, the normal commercial chromic acid plating solutions may, on the average, contain 300 g/l chromic acid. These solutions would require dilution by a factor of about 1 million to meet U.S. Public Health Service Drinking Water Standards, which specify less than 0.05 ppm for chromium.

Effluents Containing Solid Impurities From Mechanical Operation

To obtain a good-quality final finish in a metal-processing operation, whether it be an organic, metallic, or a chemical coating, it is imperative that the surface of the workpiece be completely free from oils, greases, and rust or other oxide films. Thus, it is obligatory that certain cleaning operations be performed before subsequent chemical processing. It is necessary often to subject the workpieces initially to a mechanical operation, such as tumbling, blast cleaning, polishing, or buffing. A mechanical operation can produce an effluent containing solid impurities. Water discharged from the dust collectors, tumbling, or vibratory finishing after the solids separation may contain impurities requiring chemical or biological treatment.

Effluents Containing Liquid Organic Impurities

Workpieces received in a metal-finishing plant are often covered with oils and greases left by machining operations or applied to protect their surface during storage and shipping. Oils and greases usually are removed by subjecting the workpieces to the action of organic solvents and/or inorganic alkaline cleaning solutions. Effluents generally are contaminated with these water-immiscible materials, due to dragover or batch dumping of the processing media.

The solvents used in vapor or the immersion types of degreasing—for example, the nonflammable chlorinated hydrocarbons or the flammable solvents (such as kerosene) used in emulsion cleaners—can form an emulsion in water or a floating film that not only detracts from the appearance of the water but also presents danger to all living organisms. In addition, these organic

contaminants in effluents may be flammable or may liberate toxic gases, which would also prohibit their discharge to a storm or sanitary sewer system. The BOD (biochemical oxygen demand) content may be sufficiently high to require biological treatment.

Effluents From Acid Pickling, Polishing, or Phosphating Solutions

The effluents from pickling operations yield large quantities whenever any type of metal is processed, owing to rinsing following processing or to dumping of spent processing solutions. Pickling solutions are usually strong acids. The acids are consumed by the dissolution of oxides and metals processed. The acid must be replenished and metal ion content controlled for an effective operation. In most pickling operations the solutions cannot be controlled and must be discarded. The effluent from batch dumping or from rinsing following processing is toxic because of the acidity or the metal ion content. Exposure to acid water will damage masonry and iron structures. The metal ion content of the effluent from pickling areas may be high in copper, zinc, nickel, cadmium, iron, and other heavy metals, which are dangerous poisons to all living organisms and may be fatal at low concentrations.

Effluents From Alkaline Pickling Solutions

Alkaline pickling solutions are used primarily for etching aluminum and zinc. These solutions are generally highly caustic and must be neutralized with acid or spent-acid pickling solutions to a slightly alkaline pH for the precipitation of the metal ions.

Effluents From Electroplating Solutions

Effluents from many of the alkaline plating solutions contain complex metal cyanides that must be treated to destroy or remove the cyanide radical; and the heavy metals must be removed before the effluents can be safely discharged. The primary toxic constituent of the non-cyanide-containing processing solutions, whether acid or alkaline, is the heavy metal ion content. The heavy metal ions must be removed by alkaline precipitation, electrolysis, or ion exchange. The processing solution formulation may contain complexing agents that will not allow the complete precipitation of the metal salts upon neutralization.

Effluents Containing Chromium Ions

Chromium-containing chemicals are used in many processing solutions for plating, etching, anodizing, electropolishing, and chromating. The chromium ion content of many of these processing solutions is quite high; consequently, the rinse effluents following processing are high in chromium ion, which is toxic even in the most dilute of concentrations and must be reduced to a safe level. Some of the more acceptable methods are reduction and alkaline precipitation, ion exchange, and evaporation.

Quench Water Following Cyanide Metal Hardening

These quench waters usually contain ferrocyanides in addition to the simple cyanides, and require treatment of both compounds. Paint- and metal-stripping solutions and nonelectrolytic plating systems may contain a wide variety of organic acids and salts, complexing agents, and cyanides. Both chemical and biological treatment may be required; the complexity of the problem may require consultation with the supplier of the process or with the waste-treatment specialist.

Chapter I

COMMONLY USED WASTE-TREATMENT SYSTEMS

BATCH TREATMENT

For dumped processing solutions containing high concentrations of chemicals, batch treatment may be the best system. Dumps usually are infrequent and sufficient time is available for the slow addition of the needed chemicals. Rapid treatment of concentrates may generate considerable heat, and this again may cause the release of toxic fumes. With collected floor spill, the time needed to analyze for the contents and to provide the necessary chemicals for treatment indicates the suitability of batch handling.

Concentrated process solutions containing cyanides will be handled most economically through a *batch electrolytic destruction*[1,2,3] treatment and subsequent chemical processing. High cyanide-content waste solutions should be otherwise diluted to provide a waste containing less than 1 oz/gal CN, to avoid overheating and the release of the highly toxic CNCl gas. Also, some of the metal-cyanide complexes cannot be treated rapidly with the usual chlorination. Nickel and silver cyanides, for example, require a long time for treatment and as the soluble free cyanide is destroyed in the chlorination, there is danger that the metal cyanides will precipitate as the insoluble salts and become available for further chemical destruction. Sludges containing slowly soluble metal cyanides would then result, making the solid waste discharged by the plant unsuitable for land disposal.

Batch treatment for rinse water should be considered only for small-sized plants, owing to economical considerations, and because the insoluble metal precipitates cannot be easily separated from the treated wastewater. Filtration is complex in view of the gelatinous nature of the metal hydroxides, and decantation easily disturbs the precipitated flocculent particles separated from the water in quiet condition.

Batch treatment is suitable for the neutralization of acidic and alkaline effluents and also for the treatment of cyanide- or chromium-containing wastes.

Cyanide-Containing Effluents

The dilute cyanide wastes from the rinse waters following plating operations, cyanide dips, or other cyanide-containing processing solutions are drained to a treatment tank of large enough capacity to hold the waste accumulated in one shift plus the volume of treatment chemicals. With two tanks, waste can be collected in one while treatment is taking place in the other. Each tank is baffled to provide adequate mixing and to prevent short circuiting during treatment, and each can be equipped with high- and low-level alarms.

During all stages of the treatment, the contents are continuously circulated and/or vigorously stirred to provide rapid and intimate mixing of the reaction mass. When the level alarm signals that a treatment tank is full, the wasteflow is diverted to the other tank. If plating or concentrated processing solutions are dumped very frequently, a separate holding tank should be provided. The concentrated waste from the holding tanks would be bled into the dilute waste-treatment tanks by means of a metering pump. The size of the holding tank is determined by the frequency of dumping.

Treatment consists of first elevating the pH by the addition of caustic, and second, simultaneously adding chlorine and caustic or sodium hypochlorite.[4,5] After treatment, the contents of the tank are discharged.

Manual Batch Cyanide Waste. A typical manual batch system for cyanide waste is shown in figure I-1. In operation, the circulating pump is started and the pH of the waste is adjusted by adding caustic to the system through the caustic feed pump. The pH is checked at approximately 10-minute intervals using either universal or narrow-range pH test paper. When the pH reaches 11.5, the caustic feed pump is stopped. A sample of the waste must then be collected for a determination of the cyanide content in order to establish the approximate additions of chlorine or sodium hypochlorite required. The treatment chemicals are fed continuously for a predetermined time. At the end of this time, the chemical feeds are stopped, but circulation of the batch is continued. At the end of 45 minutes, a sample of the batch is tested for residual chlorine or cyanide. If cyanide is still present, the chemical treatment is continued by starting the chemical feed pump. The batch is then tested at intervals approximating 15 minutes until it has been determined that all cyanide is destroyed. When the absence of cyanide has been confirmed, the pumps are stopped. The treated batch may then be dumped to a clarifier for settling the precipitated metal salts prior to the discharge of the treated effluent.

When the second tank has become full, the wasteflow is diverted to the now empty first tank. The batch in the second tank is then treated in the same manner.

Instrumented Batch Cyanide Waste. In the instrumented batch system, semiautomatic control is provided by the addition of pH and oxidation-reduction potential (ORP) controllers.[6] The operation is as follows:

With the pH controller switched to manual control, caustic soda is injected by the caustic feed pump into the untreated waste as it is pumped into the circulation system. The pH is raised to 11.5 initially. When the pH has been adjusted, the booster pump is started and sodium hypochlorite or chlorine is added at the desired flow rate.

At the same time, the pH instrument is switched to automatic control and, under the proportional throttling control of the pH instrument, the caustic feed pump continuously adds enough reagent to maintain a pH of 11.5 during the reaction. The pH controller is equipped with a low-pH-limit switch for alarm and is interlocked with the booster pump to stop chlorine or sodium hypochlorite feed in the event of a low-pH condition.
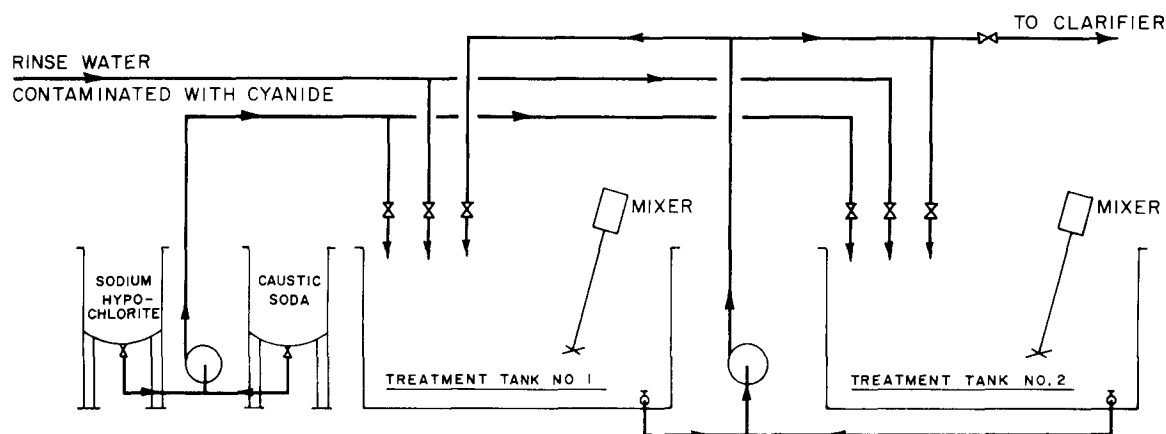

Figure I-1. Manual batch cyanide system.

The progress of the chlorination is continuously indicated by the ORP recorder-controller. When this instrument senses that the endpoint of the reaction has been reached, after about an hour, it shuts down the booster pump through a limit switch and signals the operator.

The batch continues to circulate for 30 minutes, and if the ORP recorder still shows the reaction to be complete, the treated waste can be dumped. Should the reaction be incomplete after the 30-minute mixing period, the chlorine booster pump is started and continues to feed chlorine or sodium hypochlorite until the limit switch on the ORP controller is again tripped, indicating that the reaction is complete. The pH recorder-controller will maintain the proper pH automatically during chlorination.

Kastone Process.[7,8] The Kastone process was developed by the Du Pont Company and is recommended for the treatment of sodium, potassium, zinc, and cadmium cyanide only. The solution pH is adjusted to 10.0-11.5, the solution is heated to 120-130° F, and hydrogen peroxide and formalin are added according to recommendations of the supplier, depending on a previous analysis. In approximately 60 minutes, the treatment is completed and the waste may be checked for unreacted cyanide. If it is established that all the cyanide content is treated, the waste may be decanted or filtered and discharged. The filterability of the metal solids is improved by the process, but there is greater danger for entrapment of the insoluble metal cyanides in the sludge. The chemical costs are somewhat higher with this process; on the other hand, there is no danger of generating cyanogen chloride gas during treatment. The effluent requires biological treatment, so it must be discharged to a sanitary treatment facility.

Chromium-Containing Effluents

The batch treatment of chromium is handled in a similar manner to cyanide batch treatment. The chromic acid wastes from the rinses following plating solutions, bright dips, and conversion coatings are collected in two duplicate receiving tanks alternately used for collection and treatment. As in the case of cyanide, it is desirable to provide a third tank for holding dumped spent processing solutions and a metering pump to bleed a predetermined portion of the solution from this tank into the treatment tanks containing dilute wastes.

Treatment consists of first lowering the pH by addition of acid, second, adding sulfur dioxide or sodium metabisulfite to reduce the hexavalent chromium, and third, elevating pH adding caustic to precipitate the trivalent chromium.

Manual Batch Chromium Waste. In operation, the circulation pump is started and concentrated sulfuric or hydrochloric acid is added to the batch manually or by means of the acid feed pump. The pH is checked at frequent intervals and, when it reaches 3.0, acid addition is stopped. A sample of the waste must then be collected for determination of the hexavalent chromium content of the waste in order to establish the required feed rate for sulfur dioxide or sodium metabisulfite. A procedure can be set up for this purpose, using a color comparator. For each installation, curves can be plotted for the quantity of chemical required versus hexavalent chromium.

When the required chemical feed rate has been determined, the pump is started and the previously dissolved sodium metabisulfite is added or the sulfur dioxide feed rate set on the sulfonator. The batch is then circulated continuously for about 3 hours. At the end of this time the sulfonator booster pump is stopped, but the batch is circulated for another 15 minutes.

At the end of the 30-minute period, a sample of the treated batch is tested for hexavalent chromium. If the test indicates that hexavalent chromium is still present, the treatment is continued; more chemicals are added from the sodium metabisulfite stock solution tank, or the sulfonator booster pump is started again. The batch is then tested at 15-minute intervals until all the

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hexavalent chromium has been reduced, at which time the sulfonator booster pump is stopped. Caustic is then added manually or by means of a caustic feed pump until the batch attains a pH of 8.0, at which point the trivalent chromium will precipitate out of solution. The treated batch can be discharged to a clarifier, or decanted to the sewer.

When the second tank has become full, the wasteflow is diverted to the now empty first tank. The batch in the second tank is then treated in the same manner.

Instrumented Batch Chromium Waste. A semiautomatic batch treatment system can be provided by the addition of pH and ORP controllers.[9] In operation, the pH controller is switched to acid control and acid is injected by the acid feed pump into the untreated waste as it is pumped into the recirculation system. The pH is lowered to 3.0, at which point the acid feed pump is cut off. The chromium booster pump is then started and sulfur dioxide is fed at a preset flow rate, maintained constant by the manually set sulfonator. Using sodium bisulfite or ferrous sulfate as a reducer requires controlled additions of acid to maintain the preset pH.

The progress of the reduction reaction is continuously indicated by the ORP recorder-controller. When this instrument senses that the endpoint of the reaction has been reached, it automatically shuts down the booster pump. The pH recorder-controller is then switched to alkali control and the caustic feed pump is started. When a pH of 8.0 is reached, the pH controller cuts off the caustic feed pump. The trivalent chromium will precipitate and the batch can be discharged to a clarifier to settle the precipitated chromium salts.

CONTINUOUS TREATMENT

In contrast to batch treatment, continuous treatment for rinse-water effluents allows closer instrumental control, better mixing of the reacting chemicals, and a uniform rate of flow prerequisite for the successful performance of a clarifier, usually following the chemical treatment as the first step in the liquid-solids separation to remove the precipitated metal salts.

The rinse-water streams are separated according to the various chemical treatments needed. Each segregated stream passes through a reaction tank of suitable size with mixing and reaction chambers and instrumentation to allow the required chemical feed and retention time to provide the optimum conditions for the completion of the intended reaction. Subsequently the treated individual rinse-water streams are mixed for self-neutralization, final pH control, possible polyelectrolyte dosing for best flocculation, and discharge to a clarifier or lagoon to settle the precipitates and skim potential floating solids.

Continuous Cyanide Treatment

The dilute wastes are drained directly to the first reaction tank. A separate holding tank is provided for concentrated wastes, which are slowly bled into the first reaction tank by means of a metering pump. The reaction tank is baffled to insure positive mixing and prevent short circuiting of the waste through the tank. In the first reaction tank, the cyanides are converted by the chlorine addition into cyanogen chloride, which will hydrolyze to cyanate in 10-15 minutes, at a pH of 11.0-11.5. The pH is maintained constant by the injection of caustic through the metering pump, which is proportionally controlled by the pH recorder-controller. Chlorine is fed to the system by a chlorinator or added from a sodium hypochlorite stock solution tank through a control valve. As mentioned earlier, the first reaction—cyanide to cyanate—takes place at a pH of 11.5. If required, the cyanate may be completely broken down to nitrogen and carbon dioxide gases in a second

reaction that occurs more rapidly at pH 7.5-8.0. The pH reduction is accomplished by the addition of concentrated mineral acid. The acid is fed to the reaction tank by a control valve.

From the pH adjustment tank the waste flows to a larger, baffled tank where the complete destruction of the cyanate is accomplished. Either chlorine and caustic are added to this tank, controlled by pH and ORP instruments, or sodium hypochlorite solution is fed by the ORP controller. The effluent from this final reaction tank is discharged from the plant directly to a settling tank or lagoon.

Continuous Chromium Treatment

As in the case of cyanides, continuous treatment of chromate wastes is more practical than batch treatment for plants handling large amounts of dilute wastes.

The continuous system for the treatment of chromates is basically similar to that for cyanide treatment. In operation, the dilute wastes are drained directly to the reaction tank. Concentrated wastes from the holding tank are slowly bled into the tank by means of a metering pump. The hexavalent chromium is converted to the trivalent state in the reaction tank by the addition of a sodium metabisulfite solution or sulfur dioxide. The reaction is virtually instantaneous at a pH of 3.0 or less. The pH is maintained constant by the addition of mineral acid through a control valve regulated by the pH recorder-controller. Sulfur dioxide may be fed to the system by an SO_2 feeder.

From the first reaction tank the flow of the waste is directed to the small pH adjustment tank. Here, the pH is increased to 8.0 by alkali addition. The pH recorder-controller automatically maintains the pH constant by the addition of the caustic soda solution. From the pH adjustment tank, the waste can be discharged to a settling tank for separation of the precipitated solids. Figure I-2 shows the schematic arrangement for continuous treatment of a cyanide- and chromium-containing effluent.
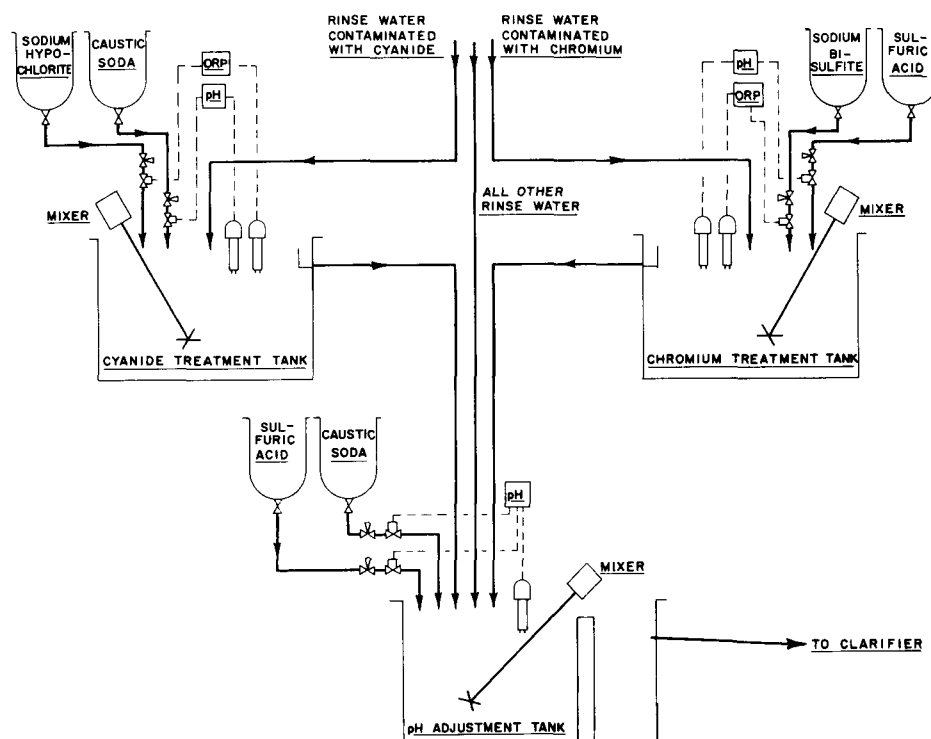

Figure I-2. Continuous treatment of cyanide and chromium.

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The advantages of the continuous system are:

● Design is simplified. Assuming the presence of only conventional metal-finishing processes with well-known chemical treatment requirements, engineering problems are minimized.

● With proper instrumentation and incorporation of safety features, the supervisory attention is minimal; therefore, no separate waste-treatment operator is needed.

The disadvantages of the system are:

● Opportunities are minimal for water saving or reuse.

● The precipitated metal salts are mixed, eliminating the opportunity for economical metal recovery from the sludges.

● Chemical costs are high because, with the metal precipitation and water hardness, solids have to be precipitated and the chemicals for pH adjustment for the various treatments can become significant.

● Unless care is exercised and complexing agents are rigorously kept out of the rinse water, meeting of effluent limits may be marginal or not possible.

INTEGRATED TREATMENT[10,11]

The integrated treatment system was devised primarily to meet the need of the plating industry for improved rinsing, and to create savings to offset the costs of waste treatment. The basic concept of the integrated system is the segregation and treatment of the waste at the source. To accomplish this purpose, the liquid film of plating solution that adheres to the part as it is removed from the bath is simultaneously treated and removed from the plated or processed part. The waste treatment is integrated into the processing sequence and no separate treatment plant is required. The system can be employed following any processing step that would result in toxic waste carryover, regardless of its position in the processing line. The simplicity and reduced space requirements of this system make it easily adaptable to existing processing lines.

In operation, a treatment wash tank is substituted for the first rinse tank following the plating operation. A treatment wash solution is recirculated continuously through this tank, where it physically removes the dragout and at the same time reacts chemically with it. The part is then rinsed with fresh water in the subsequent rinse tank. The effluent from this rinse tank is now uncontaminated with toxic dragout or precipitated metal hydroxides and requires no additional treatment.

The treatment solution is continuously recirculated between the treatment wash tank and a larger reservoir. The reservoir tank serves three major functions.

● It is the all-important buffering component in the system that neutralizes the shock load caused by sudden and irregular changes in the quantity of plating or processing solution dragout treated.

● It serves as a clarifier, settling out the insoluble metal oxides and hydroxides formed in the first stage of the reaction.

● It serves as a retention tank, providing adequate time for the desired chemical reaction, such as oxidation of cyanates to carbon dioxide and nitrogen, and treatment of nickel cyanide, silver cyanide complexes, all of which take hours for completion.

Only one reservoir tank is required; several treatment wash tanks can be served by a common reservoir tank. Various metal wastes should not be mixed if metal recovery from the sludges is the aim.

The integrated system can be completely automated, but in smaller plants it operates without the need for close control since high excesses of treatment chemicals are used in the closed loop. Relatively simple paper and spot tests are sufficient for control of the treatment process. Treatment chemicals are added either continuously or by batch as they are consumed by the toxic materials. A typical integrated system is shown in figure I-3.

The system has many advantages, including the following:

● Equipment costs are low. The equipment is integrated into the finishing line, occupying a minimum of floor space and requiring no separate waste-treatment plant.

● Supervision and control are simplified, because control is restricted to simple checks to ascertain the availability of excess treatment chemical in the system.

● Rinsing is improved, staining is eliminated, and rinsing rejects are reduced. Reduced quantities of water are used in view of the prerinse with chemicals, allowing 80-90 percent reuse of the wastewaters, since the contaminating chemicals are kept out of the rinse-water flow and no treatment chemicals are added to increase the salt content of the wastewater.

● Waste-treatment chemical cost is minimal, because one of the major chemical consumption factors—the addition of caustic or acid to bring the waste rinse water into the correct pH range for treatment—is eliminated.

● Sludge handling is simplified. The chemical system is so formulated that the precipitates are densely settled. The metal sludges are segregated, allowing simple and economical recovery of the metal values.
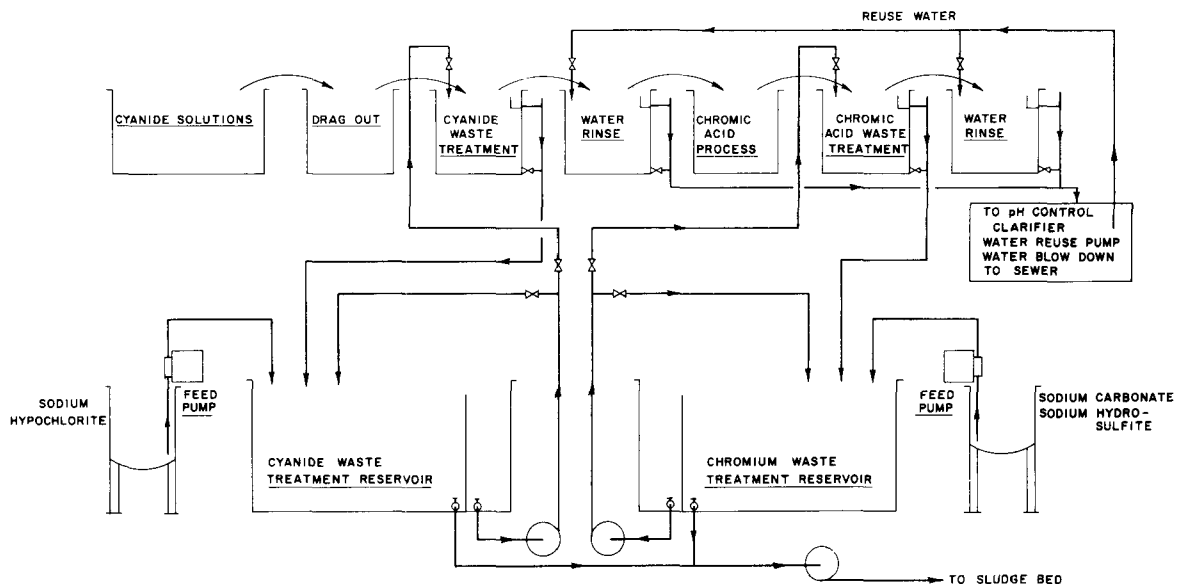

Figure I-3. Integrated treatment system.

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- The individual chemical rinse stations, operated with high content of excess reacting chemicals, provide a fast and more complete treatment. Only the dragout from the treatment rinse reaches the rinse water; therefore it is easier to meet effluent quality requirements.

The disadvantages of the system are:

- Additional rinse tanks may be required where such are presently not used, unless one of the rinse tanks in a double-rinse system can be converted to chemical rinsing.

- While the integrated rinse, if properly maintained, leads to a quality improvement in the finish, the improperly operated plant may affect the desired finish quality and may be the cause for reworks.

- The metal finisher is made responsible for waste treatment and has to attend to the maintenance of additional process solutions. It would be more convenient to leave these problems to a remote waste-treatment-plant operator.

ION-EXCHANGE TREATMENT

Ion exchange is one method of concentrating the chemical contaminants in rinse waters so that they can be treated more easily. It also makes possible the recovery of valuable materials. As a by-product, ion exchange produces deionized water that is useful in rinse tanks and in preparing new plating solutions.

Basically, ion exchange is a system for removing one ion from solution and substituting it with another ion to produce a solution that has a more desirable composition than the one being treated. The basic material involved is a granular solid known as an ion-exchange resin, which has the property of exchanging one of its ions for one of those in the solution being treated. The process itself is cyclic. The solution being treated passes through the exchanger until it exhausts the resin. In essence, the resin itself can be used indefinitely. Ion exchange can be used to concentrate rinse-water wastes that must be neutralized before discharge or, when economics dictates, it can be used to recover metals and regenerate process solutions.

Theoretically, it is possible to remove continuously the chemicals contained in the process-solution dragout from the rinse-water effluent, and to recover these chemicals in a useful form when backwashing the ion-exchange column. The backwash waters, because they are usually more dilute than the original process solution, would only have to be reconcentrated by evaporation before returning them to the process. At the same time, the rinse waters that have been passing through the ion-exchange column would be returned for repeated rinsing. Waste treatment operated in this manner becomes a closed cycle, greatly reducing the quantity of water that has to be purchased, but at the cost of chemicals that are required to backwash the ion-exchange column—that is, to free the ion-exchange resin of the process chemicals that were picked up when the waste rinse water was purified.

When an ion-exchanger installation is used for the purification of rinse-water effluent from various processes, the reclamation of the process chemicals contained in the backwash water can no longer be used for return to the original process from which they originated. In an installation of this type, the main function of the ion-exchange installation is to avoid waste treatment of large volumes of rinse-water effluent. By backwashing the exchanger, all the chemicals that would have required treatment become available in a far more concentrated form for waste treatment. The functions of the ion exchanger in an application of this type would aim to return nearly all the rinse

water to the process for repeated use and allow a simplified waste treatment with regard to the volume of the total waste to be treated. The chemical and maintenance cost of the ion-exchange installation would have to be balanced against the water savings.

In a system of this nature, consideration has to be given to the fact that the ion-exchange resin bed is capable of repeated regeneration without deterioration if it is loaded with chemicals that the resin can release on simple backwashing with the chemicals used for this purpose. With a mixed rinse-water waste stream, careful engineering is required to insure the success of the installation. Oil that may be carried by the rinse water after cleaning should be removed. Some wetting agents and organic brighteners may also foul the resin bed. It is best, therefore, to insert a carbon filter into the recirculation system to remove all deleterious organic materials before passing the waste rinse water through the ion exchanger. Another problem is the precipitated water hardness and metal hydroxides clogging the resin bed. In a pool of mixed rinse-water effluent, the pH of the stored water will determine the extent to which the metal salts in the waste may have been precipitated. The ion-exchange resin is capable only of removing ionized substances; therefore, solids such as precipitated metals and soaps will mechanically clog the resin bed. Some compounds may not be released as easily by some of the ion-exchange resin materials as some other resin formulations. It is necessary, therefore, to consider all the possible organic and inorganic materials that will be contained in the rinse water and select the resin that is least affected and easiest to regenerate for a successful installation. Figure I-4 provides a schematic presentation of an ion-exchange installation of this type.

Assuming that the precipitated metal salts are removed by previous pressure filtrations, and that the organic content of the waste stream was purified, through the use of a carbon filter, of all the materials suspected of fouling of the ion-exchange resin bed, the rinse water as it is passed through the ion exchanger is freed of all salt content and the water can be reused in a closed loop. The cation bed will remove all cations until exhausted and, similarly, the anion exchanger will remove the anions. For example, sodium, calcium, the metal ions, and trivalent chromium would
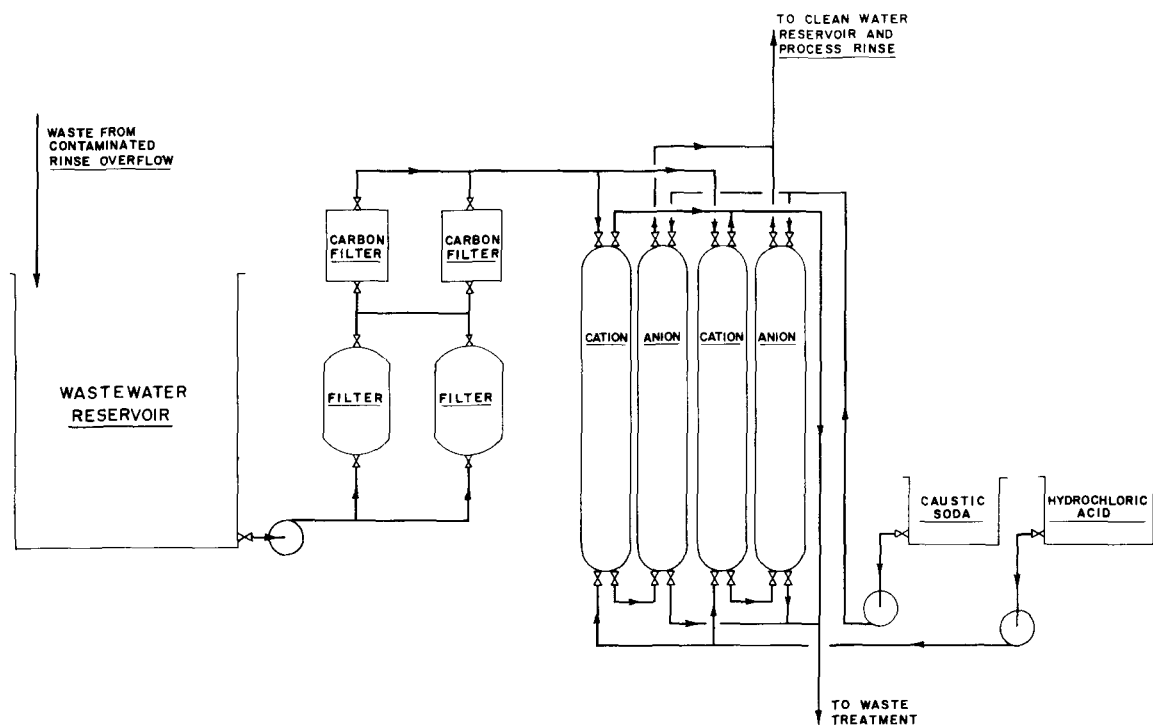

Figure I-4. Ion-exchange system.

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be retained on the cation resin, while the anion exchanger would retain the sulfates, chlorides, and so forth, hexavalent chromium, and cyanide complexes.

Each ion-exchange resin column has a certain capacity to combine with equivalent weights of the various chemicals contained either in the process solution or in the rinse water. Calculations for each installation must be made to establish the volume of resin that should be used to provide a reasonable length of time for use between backwashings. Normally, parallel ion-exchange systems are used for wastewater treatment to allow the backwashing of one while the other is on stream. The size of the installation will depend on these calculations and a certain percentage of deterioration in time should be calculated to allow for an efficiency drop of 20-25 percent in the use of the ion-exchange column.

Because the capacity of the exchanger is based only on the chemical equivalent weights of the various chemicals to be removed from the recirculated rinse water, the volume of water recirculated is immaterial. This nondependence on recirculation rate allows accelerated water recirculation for better rinsing without economical detriment. While it may not be significant that the recirculated water entering the rinse tank is desalted, because desalted water does not have buffering capacity, the fact that the flow rate can be accelerated is an advantage.

The performance of the ion-exchange system usually is monitored with a conductivity controller. When the exchange capacity of the system nears exhaustion, the salt content increases the conductivity of the water. This breakthrough of dissolved salt in the recirculated effluent is an indication that the system requires regeneration. Usually dilute hydrochloric acid is used for the regeneration of the cation exchange column, while caustic soda solution is used for the regeneration of the anion exchanger. Cyanide and wetting agents may not be retained completely and may be present in the recirculated rinse water. The complete release of chromic acid from the anion bed can be another difficulty to guard against.

The regenerant and backwash waters carry all the salts earlier retained on the resin. Usually a batch waste-treatment system is used to treat this mixed waste. Since the acid and alkali values are near balance, the regenerant and backwash waste is mixed. After cyanide treatment the chromium is reduced and precipitated in the alkaline range, the metal salts are precipitated and settled, and the clear effluent is decanted to allow the separation of the solids from the water.

The chemical treatment of the batches must be tailored to the particular installation and to the anticipated constituents of the mixed waste. Process changes and variable processing in the finishing plant may require variations in the treatment process. Complex salt formation is always a danger if the potential of iron cyanide and nickel cyanide formation is present; the cation and anion regenerant waters may have to be segregated. Complexing agents should be kept out of the effluent in a manner similar to that indicated for continuous or batch treatment. Sometimes it is necessary to pass the treated effluent through a secondary cation exchanger to remove the metal salts that could be only incompletely precipitated in the treatment.

Dumped processing solutions and floor spill are batch treated, sometimes mixed with the regenerate and backwash from the ion-exchanger system. Inconsiderate mixing of these wastes may make the treated effluent or sludges, or both, unacceptable for discharge. There is great potential hazard of creating a sludge high in slightly soluble metal cyanides, insoluble iron cyanides, or soluble metals that cannot be precipitated or separated from the water phase.

Moving-bed ion-exchange systems are theoretically similar to the fixed-bed installations.[12] Their advantage may be obvious when large capacities are needed. As shown in figure II-1, the resin is recirculated in pulses and only a short column length is used for absorption, while simultaneously regeneration and backwashing take place at other areas. Besides potentially large capacity, the greatest advantage of the moving-bed systems may lie in the fact that resin is in the loading cycle

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only for a few minutes, which permits it subsequently to be washed, then regenerated and washed again—the changes of clogging the bed with insoluble precipitates and fouling with organic compounds are greatly reduced.

The advantages of the ion-exchange treatment system are:

- Water savings are significant, up to 90 percent, owing to water recirculation. At the same time, sewer rental charges are equally reduced.

- The volume of the effluent discharged is reduced greatly, thereby allowing potential reduction of the polluting substances.

The disadvantages of the ion-exchange-type treatment are:

- Design considerations have to be very carefully weighed.

- Batch-treatment chemical costs, labor and supervisory expenses, and equipment maintenance costs are high. Sludge handling can be expensive since the metal separation can be complex.

- The investment in equipment and installation is relatively high.

Chapter II

PROCESS-SOLUTION REGENERATION AND RECOVERY
AND METAL RECOVERY

ION EXCHANGE

The best opportunities for ion-exchange systems in metal-finishing waste treatment may lie in the field of valuable metal recovery or regeneration of process solutions.[13] As an example, when rinse waters after chromium plating are passed through a cation exchange column, the system may serve to recover the valuable chromium chemicals by removing the impurities—such as trivalent chromium, copper, zinc, nickel, and iron—in the cation exchange column, the backwash waters from which would go to waste treatment. An evaporation system allows the reconcentration of valuable chemicals and the reuse of rinse waters.

An example of the maintenance of a process solution would be the removal of aluminum from a chromic acid anodizing bath, avoiding the necessity of periodic disposal of the bath.[14] Chromic acid, a strong oxidizer, will deteriorate the resin to some extent; therefore, concentrated chromic acid solutions should first be diluted with water before regeneration through an ion exchanger is attempted.

An ion exchanger receiving rinse waters from only one process can retain the desired cation or anion in a sufficiently pure condition so that the regenerant could serve as replenishment source back to the process, especially after reconcentration by evaporation. Nickel sulfate, for example, can be reclaimed in this manner.

Process-solution regeneration is perhaps the field that is economically best suited for the use of ion exchangers. The limited capacity of the ion-exchange systems and the necessity for large installations to provide the necessary salt absorbancy between backwashings to some extent has limited more common use of this type of equipment. Moving-bed ion-exchange columns overcome the common limitations assumed regarding the capacity of ion-exchange installations (fig. II-1). Successful, economical installations have been accomplished using this type of system for such process-solution recovery as bright dip solutions used for aluminum, which require resins to be able to accept high-strength oxidizing acids and which have large removal rates for aluminum, maintaining the process solution at the optimum aluminum concentration.

EVAPORATIVE RECOVERY

There are basically two systems used in the recovery of chemicals by the evaporation technique. The *vacuum evaporator* concentrates the process-solution waste at reduced temperature by depressing the boiling point, maintaining a vacuum in the evaporative vessel.[15] By reducing the pressure in the evaporator the boiling will take place at a lower temperature and the oxidative breakdown of cyanide compounds may be reduced. The *atmospheric evaporator* forces air through a chamber into which the processing solution is sprayed to accelerate evaporation rates and remove water vapor with the air that is discharged through a stack. The water removed by the vacuum evaporator can be recondensed and reused for rinsing.
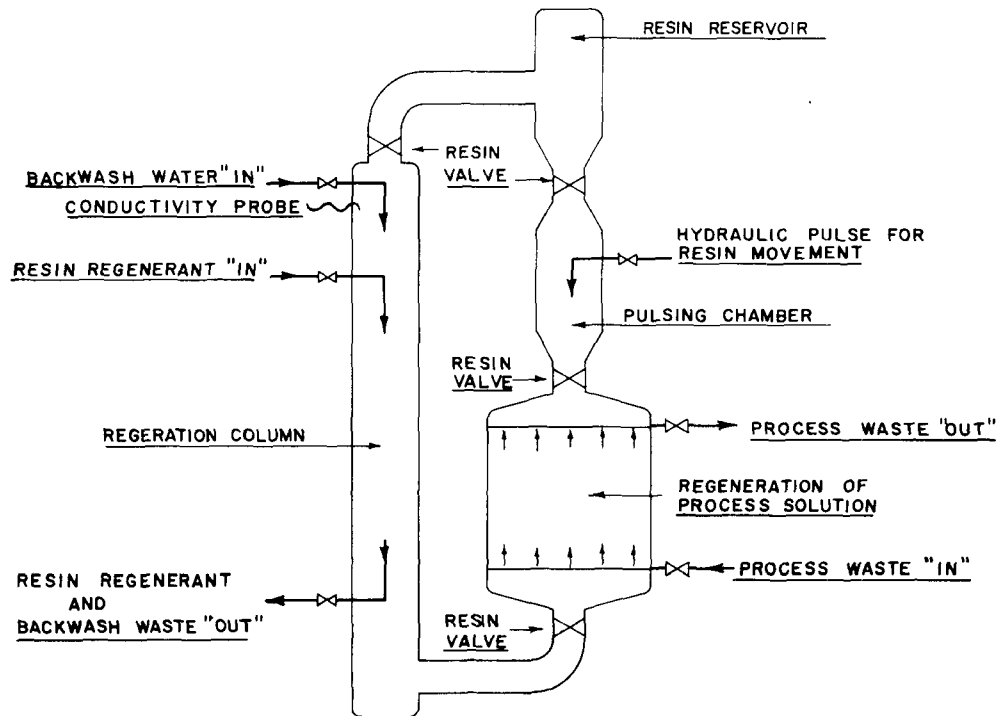
Figure II-1. Moving-bed ion exchanger.

Two modes and their variants are usually employed, depending on the number of counter-current rinse stations available and the waterflow rate required for good rinsing.[16]

Closed-Loop System

The closed-loop system is an effective way to recover cyanide, metal cyanides, chromium- and other metal-containing chemicals from plating operations so that chemical treatment of rinse water is eliminated or minimized. This technique is applied only to processing lines using countercurrent rinsing. In a typical system (fig. II-2), a single-effect evaporator concentrates flow from the rinse-water holding tank. The concentrated rinse solution is returned to the plating bath and the distilled water is returned to the final rinse tank.

In the closed-loop system, no external rinse water is added for makeup except that required by atmospheric evaporation. The only chemicals added to the plating bath are those required for replacing what is actually deposited on parts and what is lost by spillage or other accident. The system is designed to recover 100 percent of the plating chemicals normally lost in dragout for reuse in the plating cycle.

Open-Loop System

The open-loop system is adaptable to those plating installations where there are insufficient countercurrent rinse tanks, and where there is a system for partial recovery of plating chemicals. A small portion of the chemical dragout that accumulates in the final rinse tank is not circulated to the evaporator for concentration. The circulation loop through the evaporator is opened by creating another flow path for the chemical dragout. This small fraction of dragout solution not returned to the evaporator can be treated by an appropriate chemical method before disposal. A typical open-loop system with only two rinse tanks can be operated economically. In this system a small percentage of the dragout is not returned to the evaparator and must be treated.
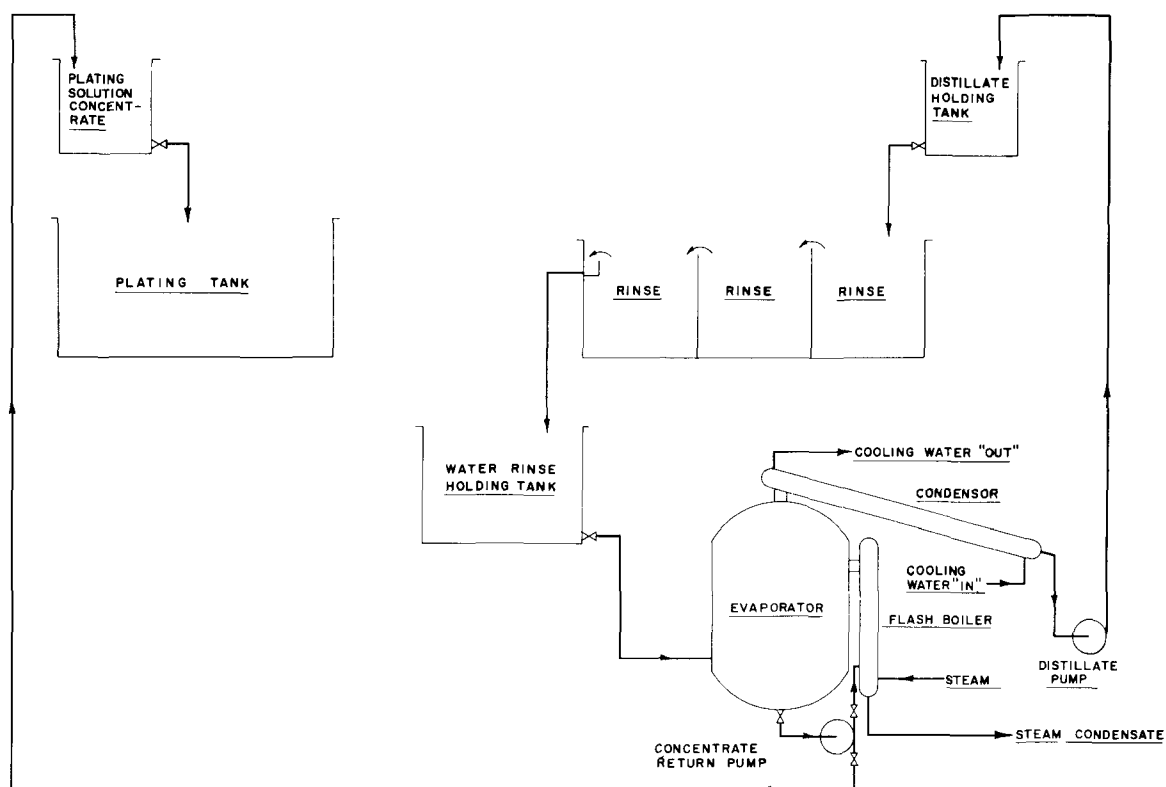
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Figure II-2. Evaporative recovery—closed loop.

REVERSE OSMOSIS

Functionally, reverse-osmosis applications in metal finishing are very similar to the opportunities available by evaporation. Theoretically, reverse osmosis aims to apply high pressure to a suitable thin membrane, overcoming the osmotic pressure and passing water through the membrane, which at the same time rejects the salt molecules and thereby separates a relatively salt-free water stream and a salt solution at a higher concentration than that in the original input.

Rinse waters from a specific process can thereby be treated, the water product returned for rinsing, and the concentrates, possibly after further concentration by evaporation, returned to the process. If the recovered water stream is sufficiently free of the dragout salts, and if a sufficient number of countercurrent rinse stations are available, the level of the original contaminant concentration can be reduced sufficiently so that a last rinse does not require treatment. Otherwise the configuration is similar to the open-loop system described for evaporative recovery.[17,18]

Suitable membrane materials for cyanide- and chromium-type rinse-water reconcentration are not yet commercially available.

Care must be exercised with reverse-osmosis systems so that the rinse water does not contain precipitated salts; otherwise, these may in time reduce the permeability of the membrane.

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METAL RECOVERY WITH THE INTEGRATED WASTE-TREATMENT SYSTEM

As discussed earlier with the various waste-treatment systems available, the integrated waste treatment aims to follow closely the processing step and is segregated with respect to the general metal-treatment process. The design theory assumes that only the metal is worth recovering to achieve economy, to reduce the sludge volume, and to avoid returning contaminants to the process and unduly increasing the metal content of the solution.

Electrolytic Recovery

After certain processes—for example, gold,[19] silver, and tin—a dragout solution is maintained as a suitable electrolyte to allow the continuous recovery of the metal in the process and to maintain the electrolytic system at such metal level that the dragout loss of the metal into the following treatment wash system is negligible economically.

Metal Recovery Values From the Sludges

The relative integrated closed loop segregates the metal in a dense sludge collected in the respective reservoir tank. Since the sludge is uncontaminated, it has a good market and can be sold to the suppliers of the plating chemicals or anodes for nearly the full value of the metal content. Especially for smaller plants this marketable sludge provides a simple and unsophisticated means to recover the dragout losses from, for example, nickel- and copper plating installations.[20,21] A significant metal loss also occurs at times of purification of these plating solutions and from filter drains. Up to 100 percent of all these wastes can be recovered easily with the integrated technique.

Larger installations may avail themselves of further savings by recovering the full metal values with a highly economical automatic electrolytic recovery plant, operating at near 100 percent efficiency, to reclaim all the nickel and copper lost. This step is obvious, for instance, for the non-ferrous metals processing plants, even though some waste sludges are mixed; for example, copper sludge containing zinc, tin, nickel, and so forth.[22]

ACID-PICKLE AND ETCH-SOLUTION REGENERATION BY CRYSTALLIZATION OR ELECTROLYTIC CONTINUOUS MAINTENANCE PROGRAMS

Processes depending on cooling or heating of the acid solutions to avoid dumping and recovering the crystallized metal salts have been known for many years. Their wider use may come in the future with added emphasis on the need to recycle and with increasing costs of sludge handling. Consider, for example, the crystallization recovery for pickling solutions for steel, the removal of ferrous sulfate, or the regeneration of ammonium persulfate copper-etch solutions as used for printed circuit boards. The removal of the copper-ammonium sulfate extends considerably the usefulness of the processing solution.

Continuous electrolytic maintenance of a desired metal concentration has been practiced for many years for pickling acids in nonferrous metal manufacturing plants. With greater emphasis on waste treatment the processes expanded, recycling the metal that was dumped earlier with significant reduction in acid-handling costs and improved processing.

Chapter III

ECONOMIC CONSIDERATIONS

From the foregoing, it will be obvious that waste-treatment costs will be greatly dependent on many factors.[23] Under plant-management control are, for example: dragout control, economical water use, good housekeeping, as well as the selection of processes from the standpoint of waste-treatment needs. Investment for solution, regeneration, purification, reduction of dumping rates, closer chemical control of processing systems—all these issues require a new look from the waste-treatment cost angle.

The engineer in charge of waste-treatment design should also consider the question from many angles:

- The design should meet not only today's requirements, but should provide the best treatment in view of the mounting restrictions anticipated in the future and should allow the safest possible margin for the client.

- Water consumption and sewer rental charges should be considered as much part of the overall cost as the chemicals used in treatment.

- Savings achieved in water-reuse opportunities and from chemical and metal recovery steps built into the waste-treatment scheme may allow economies to offset treatment costs, reducing the overall operating costs.[24]

- Increasing the supervisory and operating labor costs can be avoided only if the waste-treatment system is integral, or at least close, to the processing area.

- An extensive and expensive waste-treatment plant does not necessarily insure better treatment, more flexibility, or freedom from upsets.

- Design criteria should not be established solely on the basis of the needs of the receiving stream or the leniency or restrictive attitudes of the local regulatory agency.

A case history is reported elsewhere in detail.[25] The report covers cost comparison between three types of general waste-treatment systems as related to the cost of rinse-water treatment for the same size plants with identical dragout rates, production volumes, and other basic costs. The report is specific regarding a plating process consisting of cyanide copper strike, followed by acid copper, nickel, and chromium plating.

The following general conclusions may be drawn from the example:

Water costs and sewer rental charges are the most significant cost factor. Sludge handling is the second important cost item, followed by amortization charges.

Chemical costs for the treatment of the dragout are not a major item. When large volumes of water are processed, the precipitation of water hardness may exceed the chemical cost of treating

the chemicals from the dragout. The study does not reflect what the chemical costs of treatment would have been if solution dumping and excessive floor spill would have to be treated. Chemical costs could be a major item in a sloppy operation.

Treated rinse water due to water-reuse options may cost less than the untreated rinse water and sewer rental.

The cost comparison study did not take into consideration that all the copper and nickel are recovered in the plant under study. The actual savings far exceed the reported values. We may say, therefore, that suitable waste-treatment design in many installations may significantly reduce operating costs.

Chapter IV

SOLID-LIQUID SEPARATION, SOLIDS CONCENTRATION, AND SLUDGE DISPOSAL

INTRODUCTION

The removal of solids from the rinse water effluent is a complex problem because there are no general rules regarding the means of separation; the ability to make this separation depends on the various solids and the form in which they are dispersed. Other influences are the size and shape of the receiving vessels, the flow rate, and the content of the effluent—the mixture that causes the various particles to have a relative effect on each other and makes their separation from the water easier or more difficult.

The solids in the effluent may be large particles, such as scale, sand, or tumbling media. At the other end of the scale, they may be colloidal particles that could come from fine suspensions as used in nickel plating, cleaning, and so forth.

Regulatory interest is mainly directed toward

- The removal of precipitated and suspended metal salts, in view of their potentially toxic nature

- Esthetic appearance of the effluent, if it is discharged to the surface waters—a dye solution or dye suspension and the cloudy appearances of emulsified oil are conditions that may cause rejection of a permit

- Floating oil and debris, which are esthetically unacceptable and may be considered a pollution hazard

The following discussion will be concerned mainly with the removal of the precipitated metal salts because, in metal-finishing waste treatment, the precipitation of these metals to reduce the toxic conditions is only the first step; equally important is the removal of the precipitates from the effluent before it is discharged. In general, the removal of these suspended metal precipitates is the greater problem and requires more experience and skills than the chemical precipitation step.

Removal of the precipitated metal solids is needed because, significant metal sludge accumulation in the bottom sediment of rivers and lakes could cause toxic conditions to develop in the organisms living there even though insoluble metal precipitates have no toxic effect on the biota in the water. Also, when the effluent is discharged to the sanitary sewer, the precipitated metal salts accumulate in the sanitary sewage sludge creating possible toxic effects to the bacteria in the sewage treatment plant, soil contamination and toxic vegetation if the sludge is discharged as fertilizer on the land, and, finally, atmospheric and ash pollution if the sanitary solids are incinerated.

Waste treatment requirements usually stipulate removal of the precipitated metals, and usually set limits for both soluble metal content and the metal content of the suspended solids. In some areas, the allowable metal content is expressed as total metal content of the effluent, considering equally the dissolved and suspended metal content.

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The nomenclature of water and waste treatment distinguishes among the following:

- "Total solids" (TS) refers to the total solid content of the water after evaporation and considers the total weight of the residue after drying at 100° C.

- "Settleable solids" (SS) describes the settleable solid material content of the water. This content usually is measured by settling the sample in an Imhoff cone for 1 hour and usually is expressed in millilitres per litre.

- "Dissolved solids" (DS) include those solids which will pass through the filter and either are truly dissolved in the water or are present as colloidal solids that, therefore, cannot be separated easily from truly dissolved solids.

- "Total dissolved solids" (TDS) indicates both colloidal and dissolved matter.

- "Total suspended solids" (TSS) expresses the suspended solids content of the water under investigation, measured when weighing the residue retained on the filter after drying at 100°-105° C.

PRECIPITATION OF METAL SALTS IN WASTEWATER

The first step in the removal of metal from metal-finishing wastes is commonly called "neutralization." The term means that the pH of acid solutions is raised toward neutrality or the pH of alkaline solutions is lowered to the same condition.

Metal salts from simple inorganic compounds will tend to become insoluble in the neutral pH range, but not all metals will precipitate on neutralization and not all metals will precipitate at the same pH point and to the same extent. In view of the low discharge limits with regard to soluble metal content of a metal-finishing effluent, the initial problem in separation may be to decide what pH to aim for to reach the most complete precipitation of the metals present in the waste. Some of the metals that may be present are amphoteric, and therefore are soluble at alkaline pH; examples of such metals are aluminum and zinc. Some other metal content requires a relatively high pH to reach minimum solubility; this category would include, for example, nickel and copper.

With mixed waste streams, the best pH for the most complete separation will be that which limits the content of the most toxic of the metal salts and for which the regulatory limits are most stringent. To meet regulatory requirements, it may be necessary to segregate streams to allow the best pH conditions for the particular metals to be precipitated. As a general rule, pH 8.0-8.5 is better (although not truly neutral) than is a pH closer to 7.00. Figure IV-1 shows some typical examples of the pH conditions at which the particular metals will be found at minimum concentration.[26,27,28]

The various salts dissolved in the water also affect the solubility of the typical metal salts encountered. Table IV-1 gives a sampling of the usual metal content at various pH's if the precipitation occurs in distilled water or hard water. It will be evident from this variance that with many salts that may be encountered in a metal-finishing effluent the solubility limit at the various pH's may not be clear cut and predictable. Some of the metals may form more insoluble compounds when precipitated as carbonates rather than as the hydroxides. Chelating agents, organic acid salts, and the various wetting agents sometimes encountered in a mixed rinse-water stream may make the quantitative precipitation of the various metals nearly impossible.
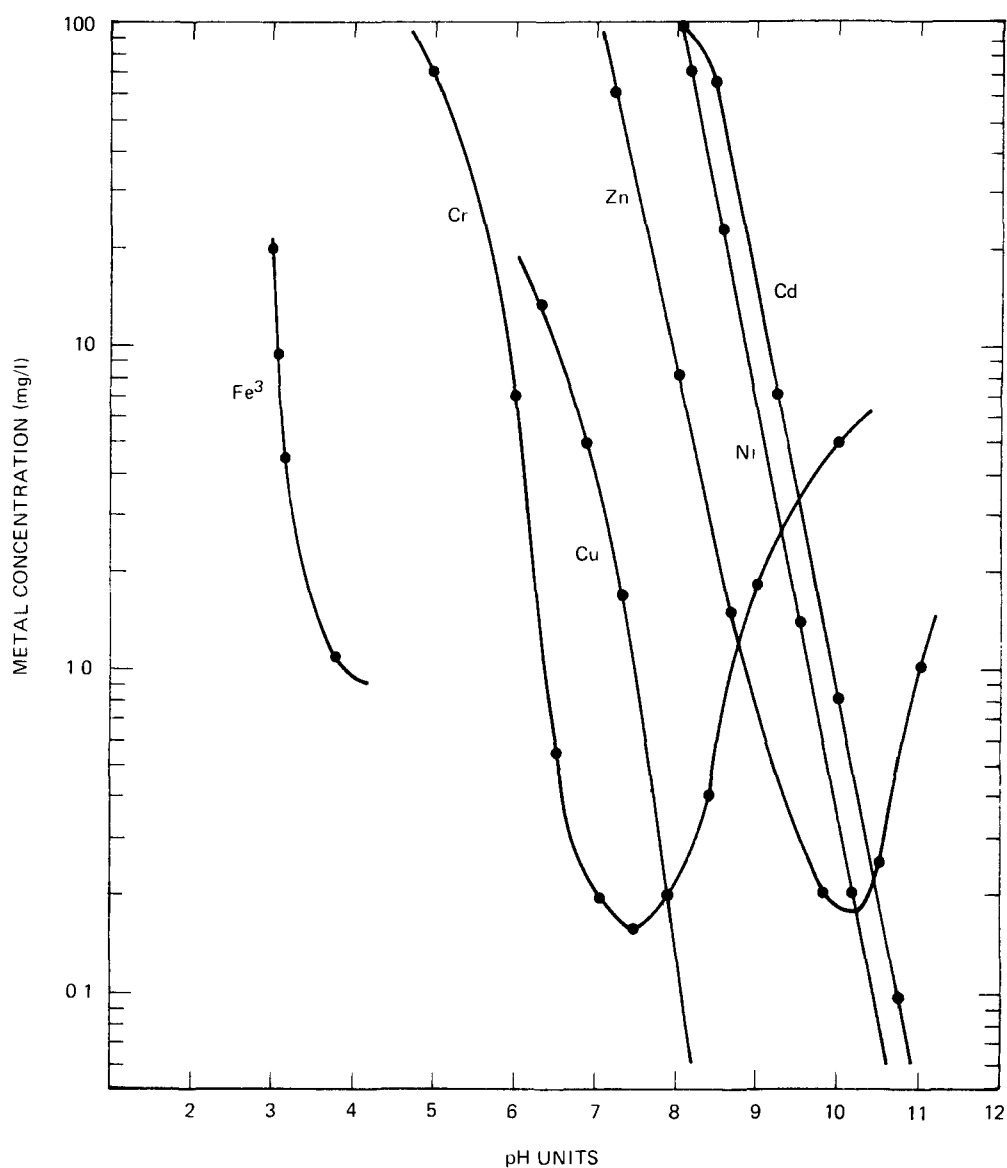
Figure IV-1. Precipitation of metal salts versus pH. See R. Weiner.[28]

GRAVITY SEPARATION OF PRECIPITATED METAL SALTS

The precipitated metals usually form a so-called floc, which is a voluminous solid particle with a specific density very close to that of water, and which therefore tends to float in the water. The flocculent particles do not have sufficient weight to settle by themselves, but must agglomerate into larger particles before they gain sufficient weight to allow settling.

Gravity settling is the most economical and simplest way to effect separation of flocculated salts. Thus, efforts must be made to cause sufficient increase in flocculent-particle size and weight to make gravity separation possible. The higher the concentration of the metal content of the effluent and the more particles per unit volume, the better the chance to effect the increase in particle size necessary for settling. It is relatively easy to effect gravity separation and precipitation when neutralizing a high-concentration waste solution, such as a dumped pickling solution relatively high in the metal salts.

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Table IV-1.—*Metal residue after precipitation, distilled and hard water*

| pH | Precipitation | | | | | | | | | | | |
| | Fe³ | | Ni | | Cr³ | | Zn | | Cd | | Cu² | |
	Distilled, mg/l	Hard, mg/l	Distilled, mg/l	Hard, mg/l	Distilled, mg/l	Hard, mg/l	Distilled, mg/l	Hard, mg/l	Distilled, mg/l	Hard, mg/l	Distilled, mg/l	Hard, mg/l
6.5 . .	0	0 8	18	19 2	18	17 8	19	18.5	19	19 2	8	11
7.0	0	4	16 5	18 9	15	13 7	18	17 8	18 5	18.4	1 3	5.8
8.0 .	0	0	12 5	10.8	5 3	7 1	1 3	9.1	15	15.2	5	2 4
8.5 . .	0	0	3 5	2 3	1.5	5	0	1 6	3 5	4.8	.2	1 7
9 0 . .	0	0	2	6	4	3 4	1.5	1.5	7	.9	0	1.2
10 0	0	0	0	0	0	.3	19 5	8 4	3	0	0	.4

Source R Weiner, *Die Abwasser der Galvanotechnik und Metallindustrie*, 4th edition, Eugen G Leuze Verlag, 1973

DESIGN FOR GOOD SETTLING[29]

The engineering of a waste treatment system has to aim both for precipitates that will tend to agglomerate, floc out, and settle, and for equipment design that lends itself to good separation.

Precipitates

The higher the metal concentration in the effluent, the larger the floc formation and the weight gain by the flocculent particles.

High concentrations of wetting agents and cleaner compounds, such as silicates and phosphates, that tend to suspend the flocculent materials and create adverse conditions should be avoided.

Precipitation with calcium hydroxide, while sometimes creating a larger volume of sludge, will tend to provide a faster settling precipitate.

Equipment Considerations

Flocculation. During neutralization it is necessary to stir the effluent to provide good mixing and to effect fast chemical reaction between the neutralizing chemicals and the contents of the waste stream. After 5 minutes, or sometimes less, the flocculent particles will start to appear; excessive stirring at this point tends to break down the small floc into colloidal material that will be nearly impossible to settle.

After neutralization is complete, 5-10 minutes should be allowed for flocculation to occur. A typical flocculation chamber would have slow agitation to permit the flocculent particles to contact each other and thereby be preconditioned for the next step.

Clarifier Design. The clarifier is basically a vessel in which the flocculent particles may settle to the bottom of the container and remain in the clarifier without being stirred and carried over the effluent weir. The basic clarifier aims for quiet conditions and laminar flow of the effluent over the effluent weir, with a minimum current affecting and stirring the contents of the clarifier.

The depth of the clarifier is important because good depth allows a floc blanket (cloud of small flocculent particles) to persist and grow, slowly settling toward the bottom of the clarifier tank, without being affected by the flow conditions near the surface of the clarifier. As the sludge content of the clarifier increases, the floc blanket, which can be 4-5 feet deep, comes increasingly closer to the surface of the clarifier until the top of the floc blanket may be disturbed by the flowing stream. As soon as this condition occurs suspended solids are carried out of the clarifier, indicating that sludge should be removed from the bottom of the clarifier to allow sufficient room for the sludge and the floc blanket to remain safely below the effluent stream. Some clarifier design parameters are shown in figure IV-2.

Polyelectrolyte Feed. The slow agglomeration of the precipitated metal floc is caused to a great extent by electrostatic charges carried by the floc particles. The same electrical charge polarity causes these particles to repel each other. The electrostatic charge most often is described as "zeta potential," an expression of the potential required to move the particles as an electrophoretic stream toward one of the electrodes. Because some particles have a positive charge and others a negative charge, there also can be a positive or negative sign indicating the zeta potential of a particular precipitate. Zeta potential close to neutrality is the desired condition for floc aggregation.

Polyelectrolytes are long-chain, organic molecules that have the capability, owing to their filamentous-polymer form, to bridge and neutralize the potential differences between the various floc particles and, as a filament, tie these particles together[30] (fig. IV-3). The charges of available poly-
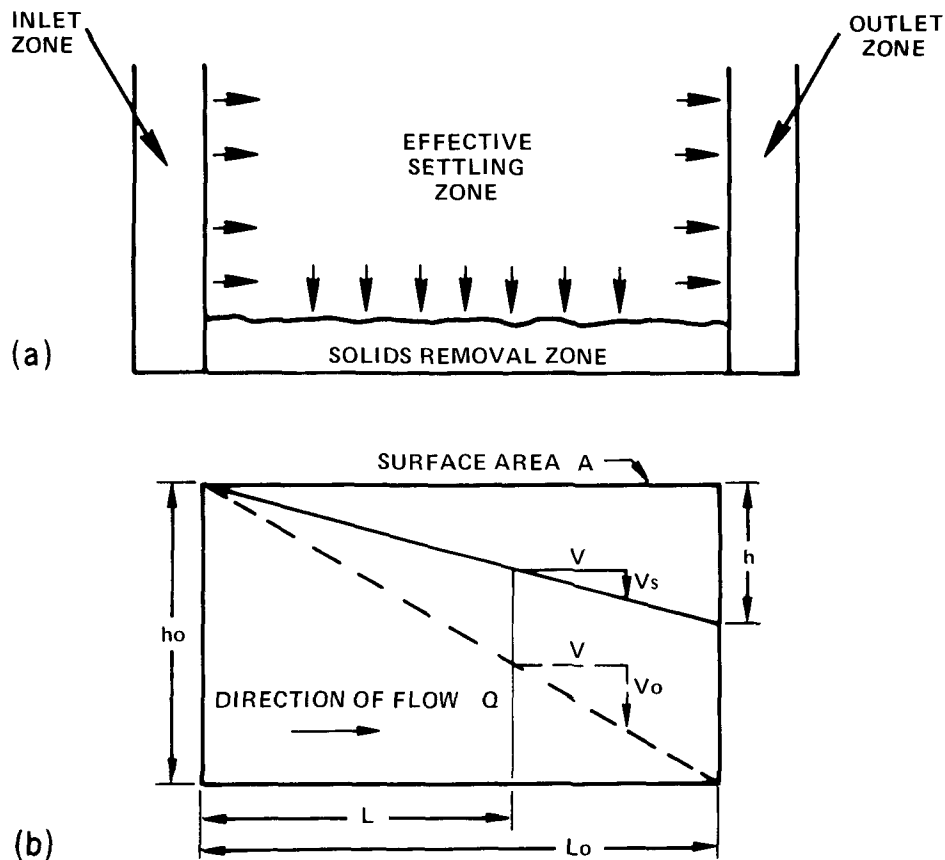

Figure IV-2. Parameters of concern in the design of a clarifier. (a) Functional zones in an idealized sedimentation basin. See R. Weiner.[28] (b) Idealized settling paths of discrete particle in horizontal flow tank. See Burns and Roe.[29]
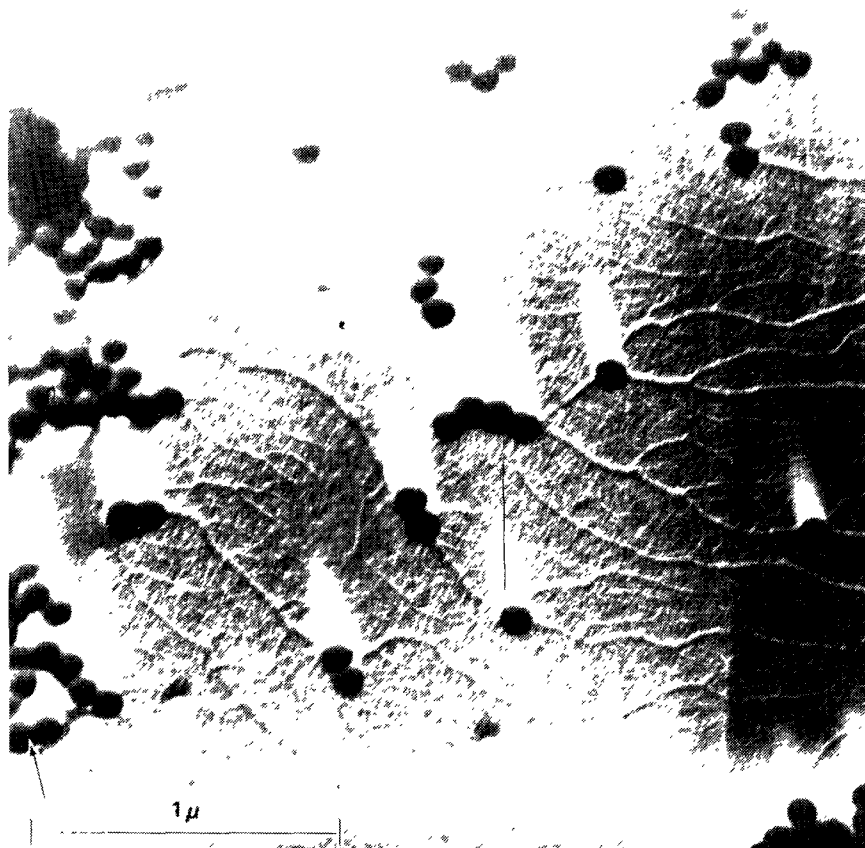
Figure IV-3. Electron micrograph of polystyrene latex and a cationic polymeric flocculent. From Ries and Meyers.[30]

electrolytes appear to be different. Negatively charged, positively charged, and neutral polyelectrolytes can be distinguished, and the difference can be significant. An empirical procedure normally is used to establish which particular polyelectrolyte to use, in what concentration, and under what condition. The empirical test is the so-called jar test, which relies on slowly stirring a container of flocculent particles, timing the settling rate of the floc and the volume of settled material, and comparing the performance of one polyelectrolyte addition with another or the concentration of one addition with more or less of the same material. As a rule, an addition of ½-1 mg/l polyelectrolyte is found best for metal-finishing effluents. Excessive amounts of polyelectrolyte can cause harm as great as the improvements that may result from proper use.

Since polyelectrolyte feed is creating additional concern and additional cost, it is used only when the settling problem cannot be solved without this aid.

Coagulants. Some of the metal precipitates form very good hydroxide floc, capable of removing other solids by adhesion. When the waste stream is very dilute, or when some content of the waste has to be removed owing to its colloidal nature or to its organic content of large molecules that cannot be separated because they are soluble, coagulants are added to the waste stream to provide additional flocculent precipitate. Most often such salts as ferric sulfate, ferric chloride, or aluminum sulfate are used in the range of 100-300 mg/l as coagulant additions to the waste stream (fig. IV-4 and IV-5).

It will be evident that coagulant additions greatly increase the amount of sludge to be handled as a final solids removal step. The usual metal content of a metal-finishing effluent stream is far
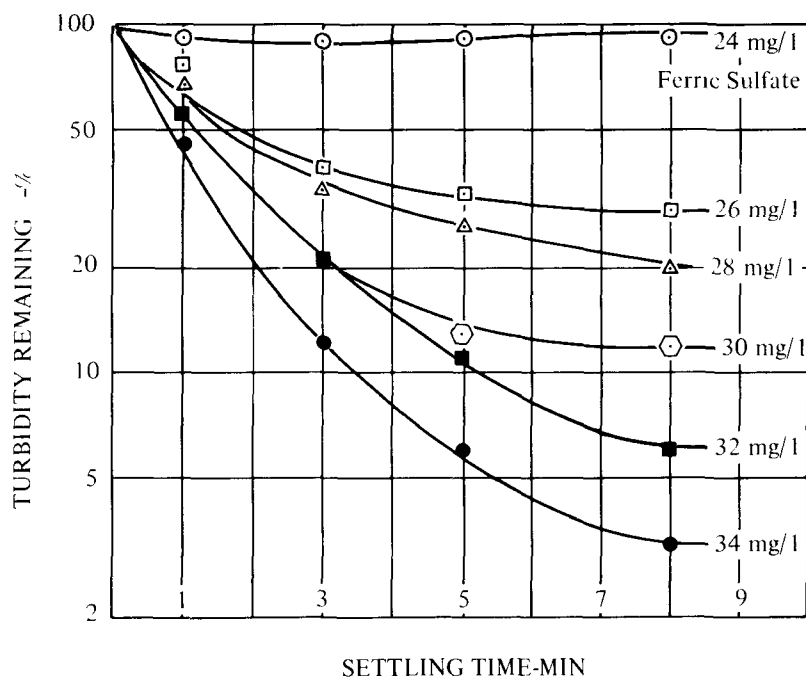
Figure IV-4. Coagulations and settling time versus concentration of coagulant.
See Burns and Roe [29]

less than the quoted quantities of metal that are fed as coagulant to be subsequently precipitated and settled with the metal that is present. As the metal salts precipitate, the anion becomes free; therefore, the pH tends to be lower when coagulants are added. Either the initial pH should be high enough to allow for this depression of the pH, or additional alkali has to be provided. With these coagulant additions, large volumes of total flocculent precipitate are created. If the mixing of the coagulant into the waste stream for subsequent flocculation is not designed carefully, all the benefits that were to be gained thereby can be easily lost.

Other Considerations. As the flocculent particles coalesce and settle to the bottom of the clarifier, additional sludge settling occurs and a sludge slurry is slowly formed. To avoid handling a very thin, dry-solids-content sludge, water has to be squeezed out of the slurry so that the dry solids content will increase. Normally, the sludge accumulated on the bottom of the clarifier contains 1-2 percent dry solids. "Dry solids content" is an expression of the metal salt content of the wet sludge, and is established after the water is filtered out and the wet filter cake is dried in an oven for 2-4 hours at 100° C.

Aging is a very important factor in increasing the dry solids content of the accumulating sludge. The greater the depth of the clarifier, the greater the capacity in relation to the accumulating total solids, and the more days the sludge may accumulate and age on the bottom of the clarifier.

Typical design criteria for the sizing of the clarifier would provide for 4 hours' retention time for the wastewater and 1 weeks' retention time for wet sludge accumulation.

IMPROVED CLARIFIER DESIGNS

Solids Contact Clarifiers

Solids contact clarifiers (fig. IV-6) are clarifiers with mechanical aids to help the flocculent particles make contact with each other and with provisions for possible addition of polyelectrolytes and for their contact with precipitating floc. Some of these clarifiers slowly agitate the floc blanket
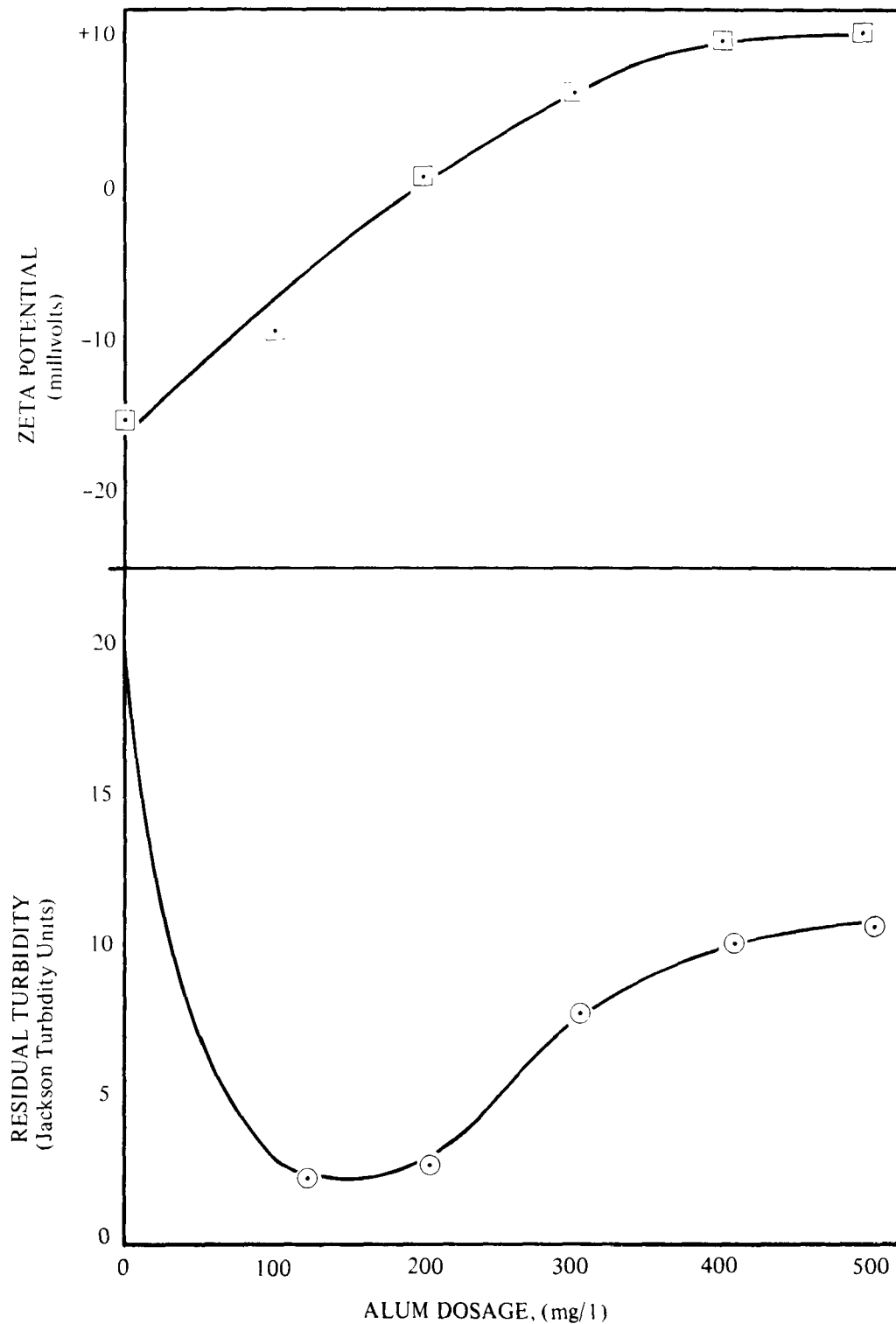
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Figure IV-5. Coagulation and particle removal versus coagulant and zeta potential. See Burns and Roe.[29]

and have provisions for polyelectrolyte addition. Others lead the incoming effluent carrying the freshly precipitated floc through the floc blanket before the effluent is allowed to leave the floc-blanket area, using the flocculent cloud somewhat as a filter to trap the small incoming particles and filter them out of the effluent stream. If the floc blanket is dense and cannot be lifted out of the

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EFFLUENT COLLECTOR FLUME

AGITATOR

CHEMICAL FEED INLETS

INFLUENT

SKIMMING SLOT

EFFLUENT

SLUDGE BLOW OFF LINE

SAMPLE CONNS.

SWING SAMPLE INDICATOR

SLUDGE CONCENTRATOR
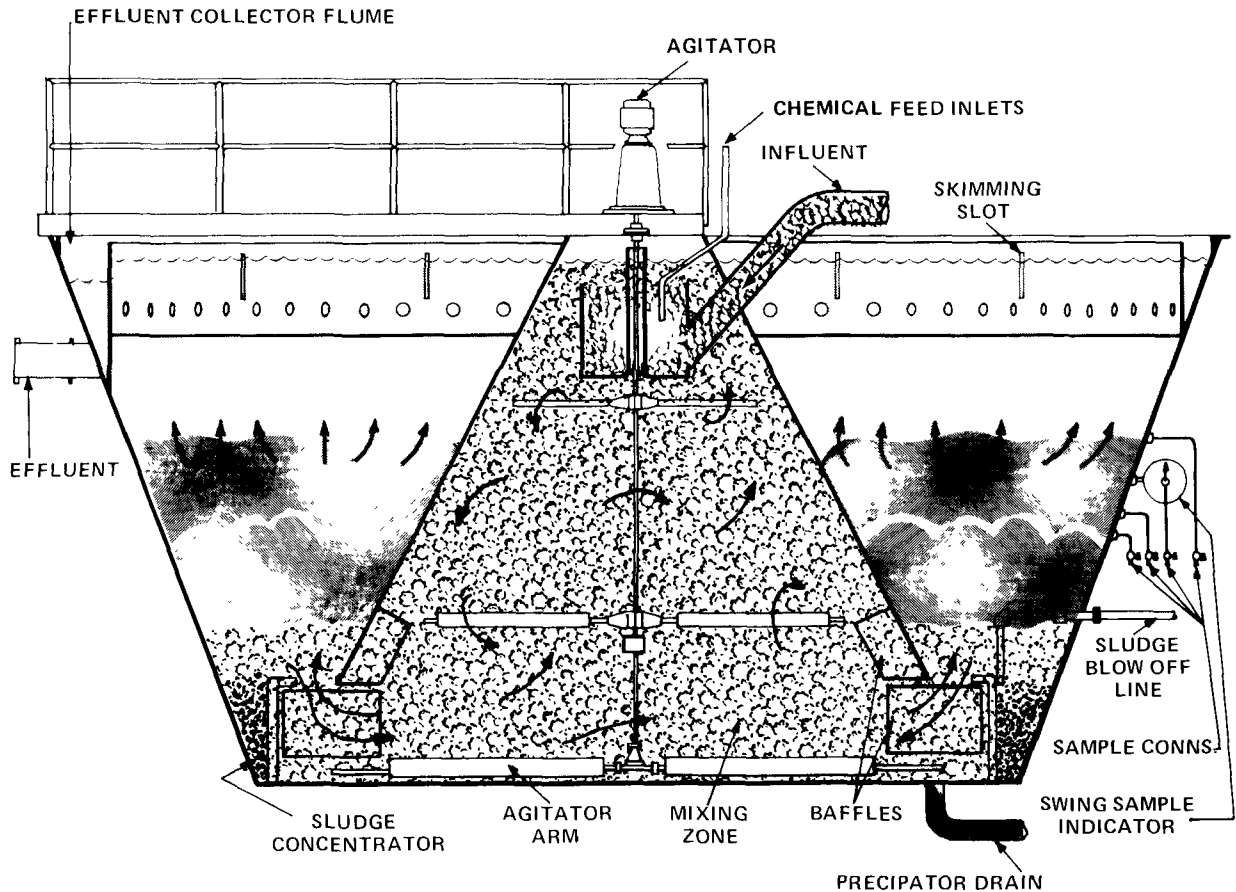
AGITATOR ARM

MIXING ZONE

BAFFLES

PRECIPATOR DRAIN

Figure IV-6. Solids contact clarifier with sludge blanket filtration. (Courtesy of the Permutit Co.)

clarifier, since it is isolated from the flowing stream on the top of the clarifier, the floc blanket can be used most efficiently as a filter.

Tube Settler and Lamella Thickener Systems

Tube Settler. The tube settler, a system first developed by the Neptune MicroFloc Co., is based on the theoretical concept that if the path of the settling particle is shortened, and the bottom of the container is brought close to it, the settling and separation of the particle will be accelerated. These designs allow a significant reduction in the size of the equipment owing to the inclined tubes that reduce the distance particles must fall to be removed. The clarifier design can be changed to shorten retention time to approximately 1 hour, while the true design parameter is the 1.5 gal/min/ft^2 rising rate of the floc particles. The tube settler allows sufficient contact to get good filtration of the rising particles through the floc blanket. Second, there is a sludge collection area sufficiently large to provide time for aging of the sludge. A conveyor system is provided to move the sludge to the discharge hopper, from which it can be discharged automatically by either pumping or gravity. Finally, tube modules impede the floating out of the suspended solids from the clarifier because the even flow through the clarifier is closely regulated with an extensive effluent weir design, and because the suspended particles can settle faster if floating in the tube modules since the bottom of the individual container (the tube) is brought very close. Because the tubes are inverted at a 60° angle, the accumulating and settled sludge is discharged automatically as it slides down the incline into the sludge collection area (figs. IV-7 to IV-11). This design is very efficient for metal-finishing waste-treatment effluents.
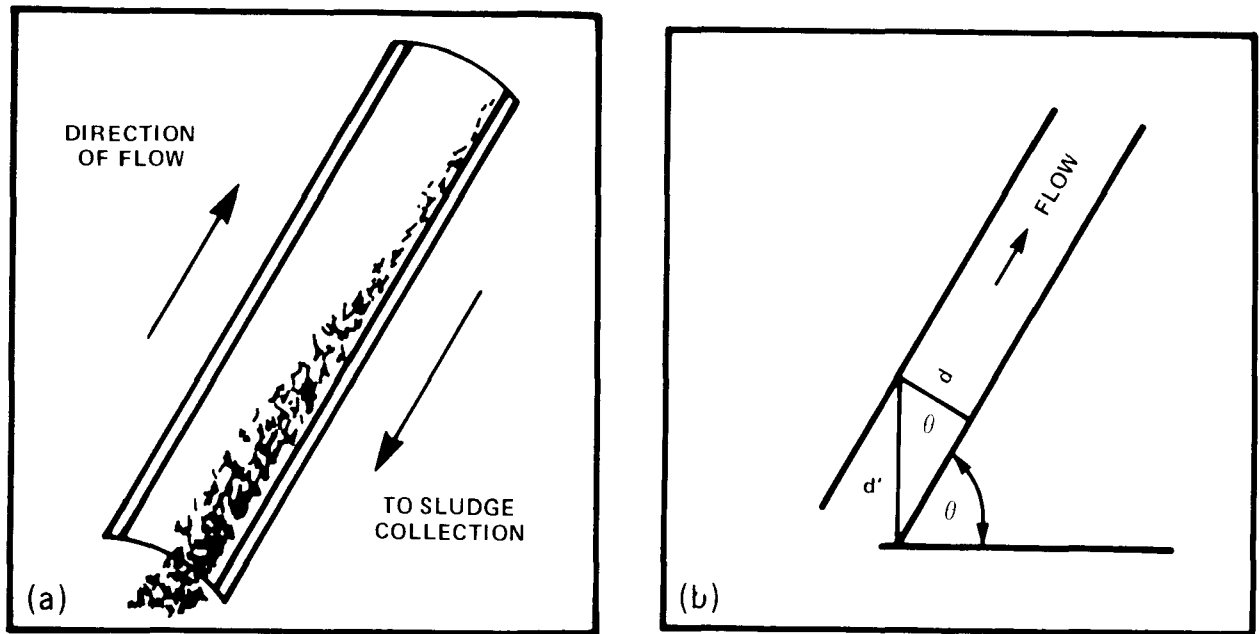
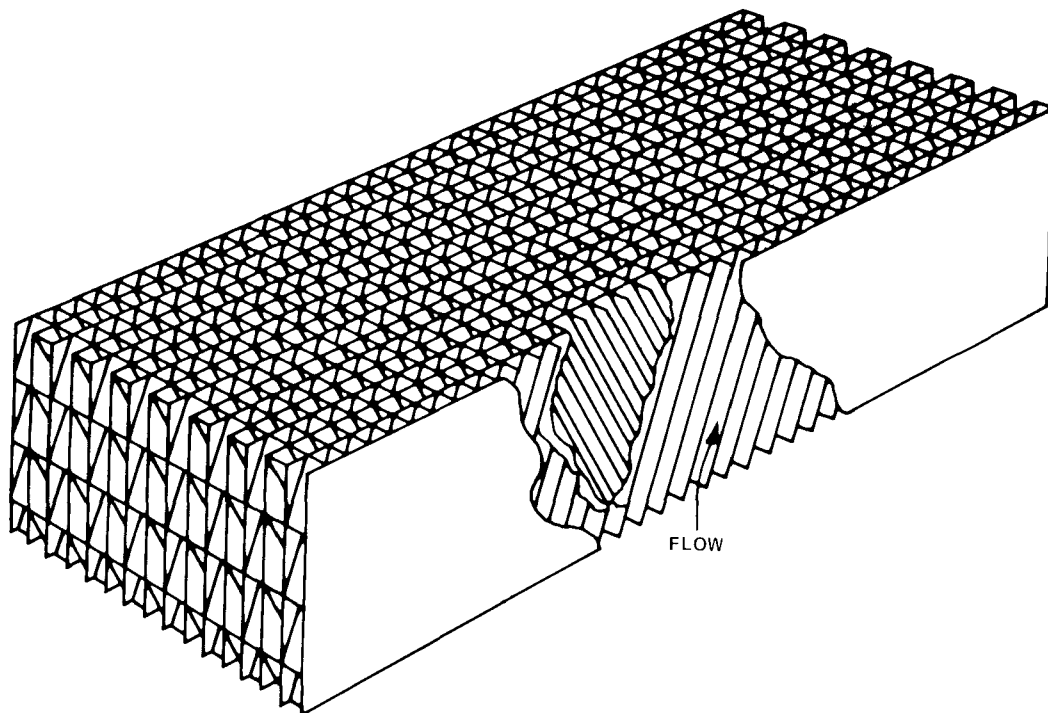Figure IV-7. Tube settlers: (a) flow pattern; (b) inclined tube. (Courtesy of Neptune MicroFloc, Inc.)

Figure IV-8. Module of steeply inclined tubes. (Courtesy of Neptune MicroFloc, Inc.)
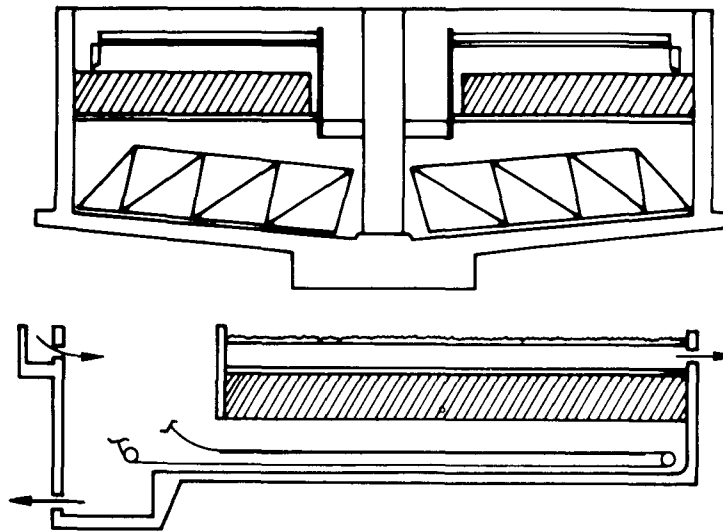
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Figure IV-9. Tube settlers in existing clarifier. (Courtesy of Neptune
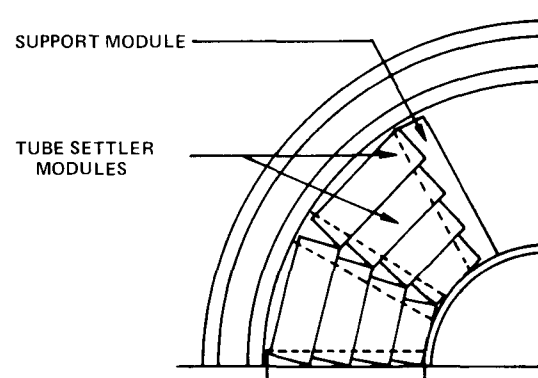MicroFloc, Inc.)

Figure IV-10. Plan view of modified clarifier.
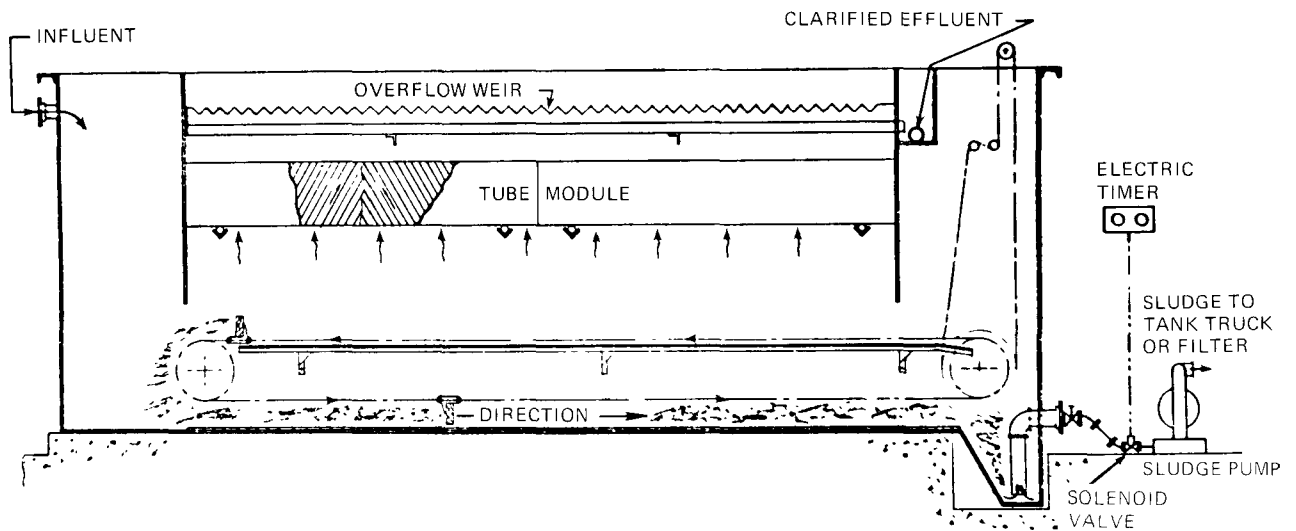(Courtesy of Neptune MicroFloc, Inc.)

SUPPORT MODULE

TUBE SETTLER
MODULES

Figure IV-11. Tube settler. (Courtesy of Lancy Laboratories, Division of Dart Industries, Inc.)

Lamella Thickener. The Lamella thickener (fig. IV-12) was introduced to this country by the Swedish Axel Johnson Company and their U.S. subsidiary, the Parkson Company. The Lamella thickener operates by separating the feed, sludge, and effluent and allowing the sludge particles to slide down the 55° incline and fall through a quiescent zone into a sludge hopper in the bottom. The sludge is further thickened in the hopper by use of a plate vibrator before being withdrawn by pumping or gravity. The effluent flows out the top through flow-control orifices, which evenly distribute the flow between plates. The Lamella thickener is best applied for new settling basin applications because it comes in a self-contained unit with attached flocculator.

Lamella thickener designs allow a further reduction in the size of the necessary equipment over tube settlers, because the clarified water (effluent), the feed (influent), and the sludge (underflow) are completely separated as they enter or exit the equipment. The sludge does not have to fall through the feed to be removed as with a tube settler. Thus, the entire horizontal projected surface area of all the plates becomes the effective settling area. The result is a significant reduction in the size of the equipment compared with a conventional clarifier, because the Lamella thickener can be designed for a flow rate of 4-5 gal/min/ft^2 of projected settling area.
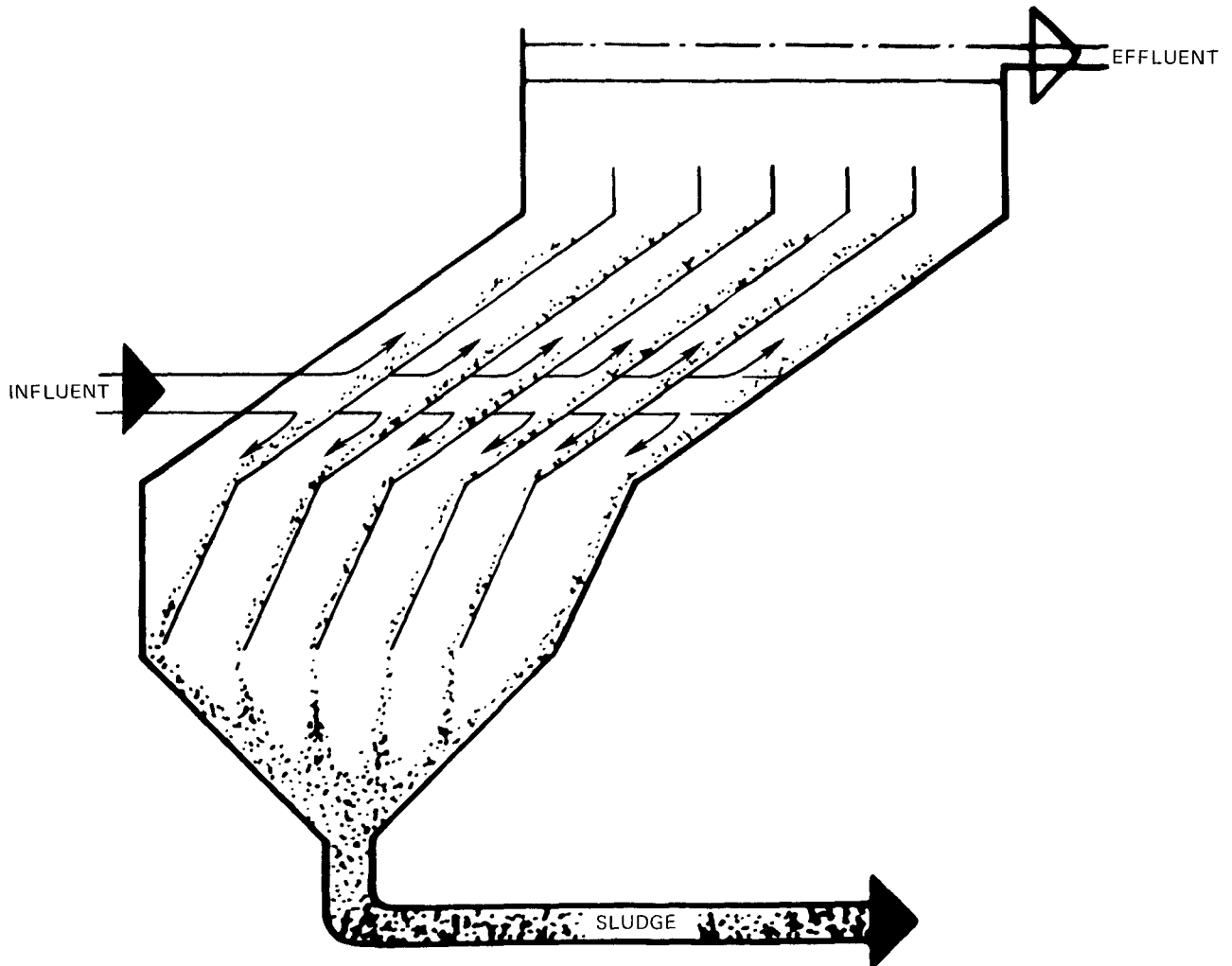
Figure IV-12. Lamella thickener. (Courtesy of Parkson Corp.)

SLUDGE THICKENING

Subsequent handling of the sludge accumulated and removed from the clarifier requires the removal of additional quantities of water because the sludge will have only 1-2 percent average dry-solids-weight content. The magnitude of the problem and the importance of sludge thickening can be perceived more clearly in terms of the volume of sludge generated in metal finishing.

A dry weight content of 1-2 percent means 50-100 times the weight in the water to be moved when disposing of sludges from metal-finishing operations. For example, in aluminum finishing approximately 1.5 percent of the aluminum processed will be dissolved and will remain in the metal-finishing waste-treatment system of a plant anodizing aluminum extrusions. A plant processing 100,000 pounds of aluminum per week therefore will dissolve 1,500 pounds of aluminum, which will form 4,500 pounds of aluminum hydroxide upon neutralization. If the plant can only dewater the sludges from the waste-treatment system to 2 percent dry weight content, there will be 4,500 pounds of dry solids multiplied by 50—that is, 225,000 pounds of sludge—for disposal for each 100,000 pounds of aluminum processed. The ratio is no different for the other processes, except where metal removal is not as great. On the other hand, the iron sludges are less easily dewatered, and chromium-containing processes, owing to drag-out, create far more metal waste to be disposed of than does the aluminum-processing example cited.

Minimizing sludge-handling problems can begin early in the processing step—hence this discussion of the value of process solution regeneration and solution and metals recovery. Because sludge handling is the most expensive part of metal-finishing waste treatment, sludge elimination in the engineering stages is the best design aim that can be followed.

Very little can be done to minimize sludge-handling problems if the waste-treatment plant is designed just to follow the traditional chemical processes without attention to segregation for the best and most economical solutions to sludge-conditioning problems, as well as for the chemistry of the various treatment processes. There are various ways in which the sludge-conditioning costs can be greatly minimized, of which the following are only a few:

- Segregated treatment of concentrated dumped processing solutions—such as waste pickles, chromate dips, and aluminum-anodizing solutions—will allow simple and inexpensive thickening of these sludges without further effort. For example, waste from an aluminum etch or dumped anodized solution can be easily conditioned so that it will have 20 percent dry weight content, instead of the 2 percent discussed earlier, by neutralizing the batch dump separately. Actually, an aluminum-processing solution containing more than 4 oz/gal of aluminum will jell because there is not sufficient water content to complete the neutralization reactions and provide inert sludge. As sludge from such waste does not have to be dewatered, it is similar to a concrete paste; if not discharged it can harden in the neutralization tank to a rocklike consistency. The same process solution discharged with the rinse water, on the other hand, will create additional costs owing to handling through the clarifier, sifting out of the flocculent material, settling, sludge pumping, and, finally, thickening.

- Segregation of the individual rinse waters and segregated precipitation of the metals, as practiced in integrated waste treatment, allows simple and inexpensive metal recovery. In addition, sludge in the integrated system—since the metal hydroxides are allowed to settle and are kept in the closed system for weeks or months—will not only grow into large clumps, but will age to the extent that the accumulated sludges can be shoveled from the container. The integrated treatment is concerned to a great extent with reducing sludge-handling costs. For this reason, the precipitation reaction is so designed that the precipitates are not flocculent material holding on to an extensive sheath of water molecules; if possible, precipitation occurs in the form of the oxide of the metal—for example, cupric or cuprous oxides in copper precipitation. In these instances, sludges with 50 percent dry weight content are not uncommon.
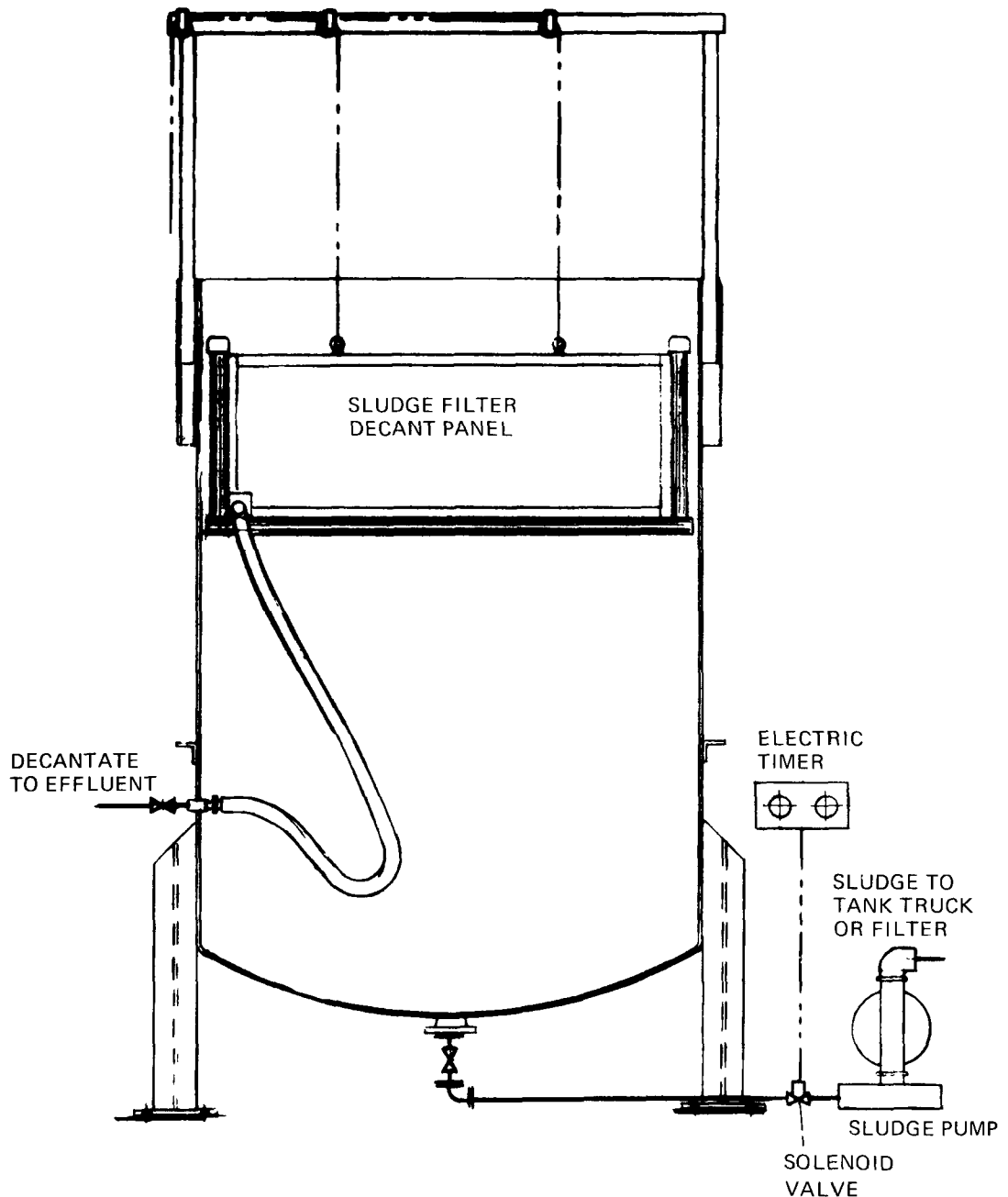
Figure IV-13. Sludge filter tank. (Courtesy of Lancy Laboratories, Division of Dart Industries, Inc.)

● Countercurrent rinsing also will greatly reduce the dilution of the wastewater; thus, it tends to increase the flocculent metal content in the clarifier, yielding a significantly higher dry-solids-weight content in the sludge subsequently removed.

The first step in sludge thickening may be a simple and inexpensive sludge-holding tank into which the sludges removed from the clarifier are pumped and allowed to settle and age further. If sufficient time is available, because the sludge is removed from the clarifier only two or three times a day, the clear supernantant water in the gravity sludge-holding tank may be decanted. Care must be exercised that the settled sludges are not stirred up; decanting must be slow, and only sufficient water must be removed to allow room for the subsequent wet sludge discharges. As one sludge layer

is deposited on top of another, water is squeezed out from the sludges by the accumulating weight and considerable aging occurs, allowing thickening of the sludges so that the 1-2-percent dry-weight-content sludge originally removed from the clarifier may be dried by water decantation to 5-15 percent dry solids content. Sludge with a 15-percent dry solids content is reasonably thick and can be compared to a thick mud.

A proprietary system developed by Lancy Laboratories uses a horizontal dewatering technique, which allows somewhat simpler dewatering than does manual decantation (fig. IV-13) and yields an even thicker sludge. The design is based on the fact that metal hydroxides are slimey precipitates and clog all filter areas if pressed into them. Horizontal dewatering—as it occurs in a porous concrete-block sludge filter (fig. IV-14) in a porous plastic-walled container, or through the use of a porous plastic decant panel inside the sludge holding tank—allows gravity water removal and evaporation by capillary seepage into the porous walls of the filter.[31] These vertical walls or internal decant panels do not clog, even though the metal hydroxides are slimey and prone to clog porous membranes, because no pressure is allowed to develop. The water separation surfaces are designed for a maximum water head of 3 feet. If any solids accumulate on the filter surface, they can be removed easily by mechanical means.

Dewatering to more than 15-20 percent dry solids content should be avoided in the sludge thickener because the sludges will not be pumpable. A 15-20 percent dry-solids-content sludge can be hauled in a tank truck or in drums to a disposal site and dumped. The sludge will dry completely within days.

Centrifuges also will provide a dry-solids-content sludge—usually 15-20 percent. Sludges should be of approximately 2-5 percent dry solids content before centrifuging for best performance. The liquid waste discharged by the centrifuge during the solids-liquid separation processes will be high in suspended solids; therefore, it is best to direct this discharge back into the clarifier for resettling and separation of the liquid and solid phases.

FILTRATION OF SLUDGES

Vacuum Filter

The most commonly used filter for metal-finishing sludges is the vacuum filter (fig. IV-15). As explained earlier, metal hydroxides are not easily filtered, and it is general practice to conduct some filtration tests on typical sludge samples before deciding whether a certain filtration technique will be successful. The sludges should be preconditioned, and a dry solids content of 2.5-5 percent is necessary for reasonable chance of success. The usual dry solids content of the cake discharge from the vacuum filter will be in the range of 20-25 percent.

FRENCH DRAIN TILE
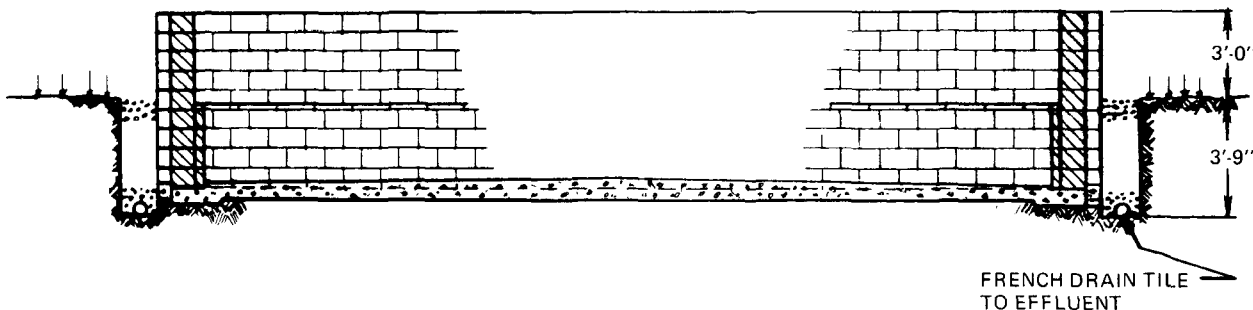TO EFFLUENT

3'-0"

3'-9"

Figure IV-14. Concrete-block sludge filter. Courtesy of Lancy Laboratories, Division of Dart Industries, Inc.)
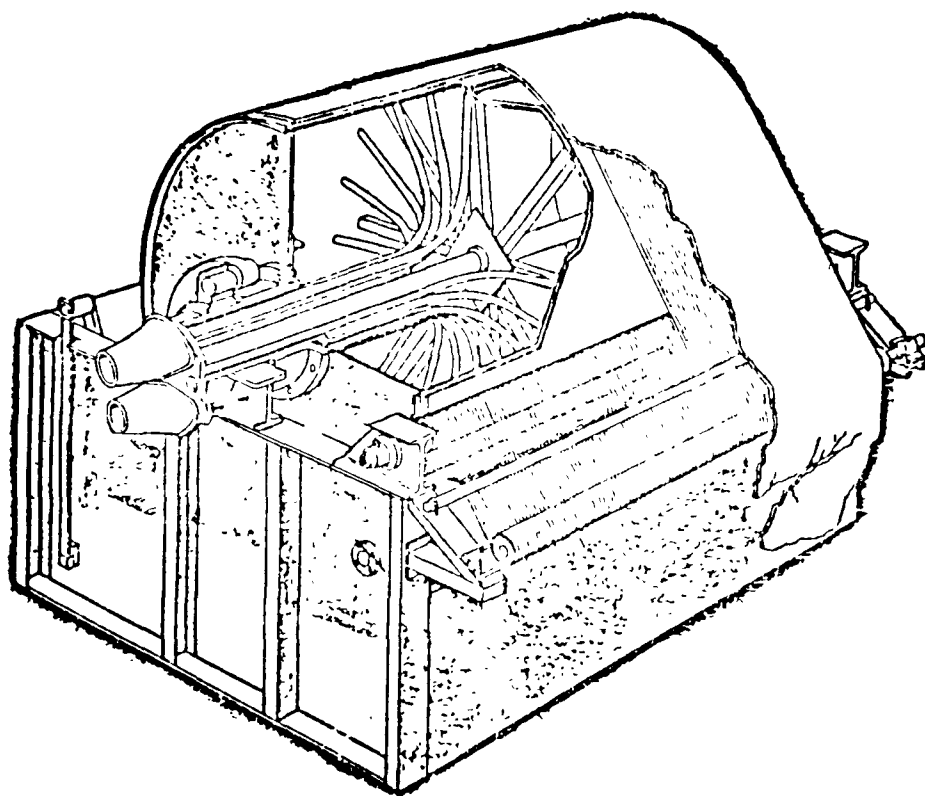
Figure IV-15. Vacuum filter. (Courtesy of Filtration Engineers Division, Ametek/Process Equipment.)
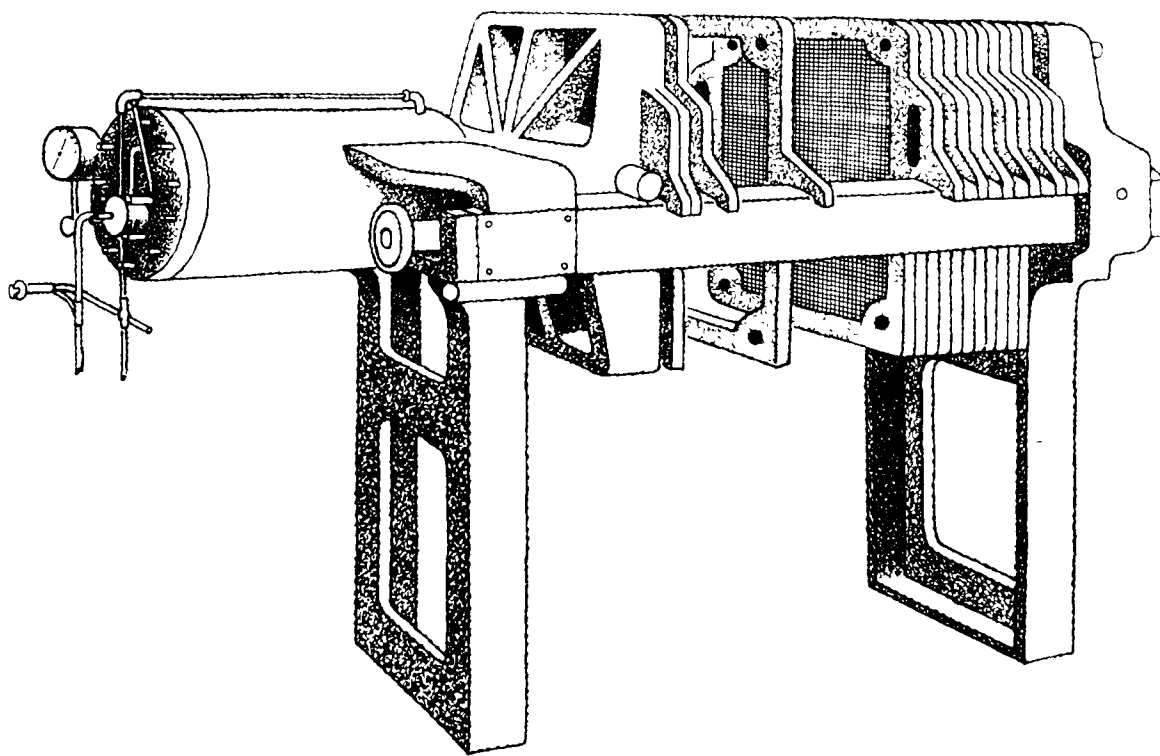

Figure IV-16. Plate and frame pressure filter. (Courtesy of Johns-Manville Corporation.)

Pressure Filters

The following two types of pressure filters are used in industry:

● Plate and frame filter (fig. IV-16)

● Chamber filter (fig. IV-17)

The operation of both filter types is similar. The chamber filter differs mainly in that it allows far greater cake thickness to be developed and, therefore, for large operations where the sludge volume warrants, the chamber filter will be the preferred equipment. Chamber filters were developed in Germany for these types of applications, and automatic cake discharge filters are available for large capacity applications. The pressure filter can further reduce the water content; 40-60 percent dry solids content can be achieved, depending on the type of metal hydroxide sludges processed. (See also fig. IV-18.)

The dry cakes from these various mechanical filters can be discharged into dump containers. The sludge from the chamber filter will be sufficiently dry to be conveyorized into dump trucks.
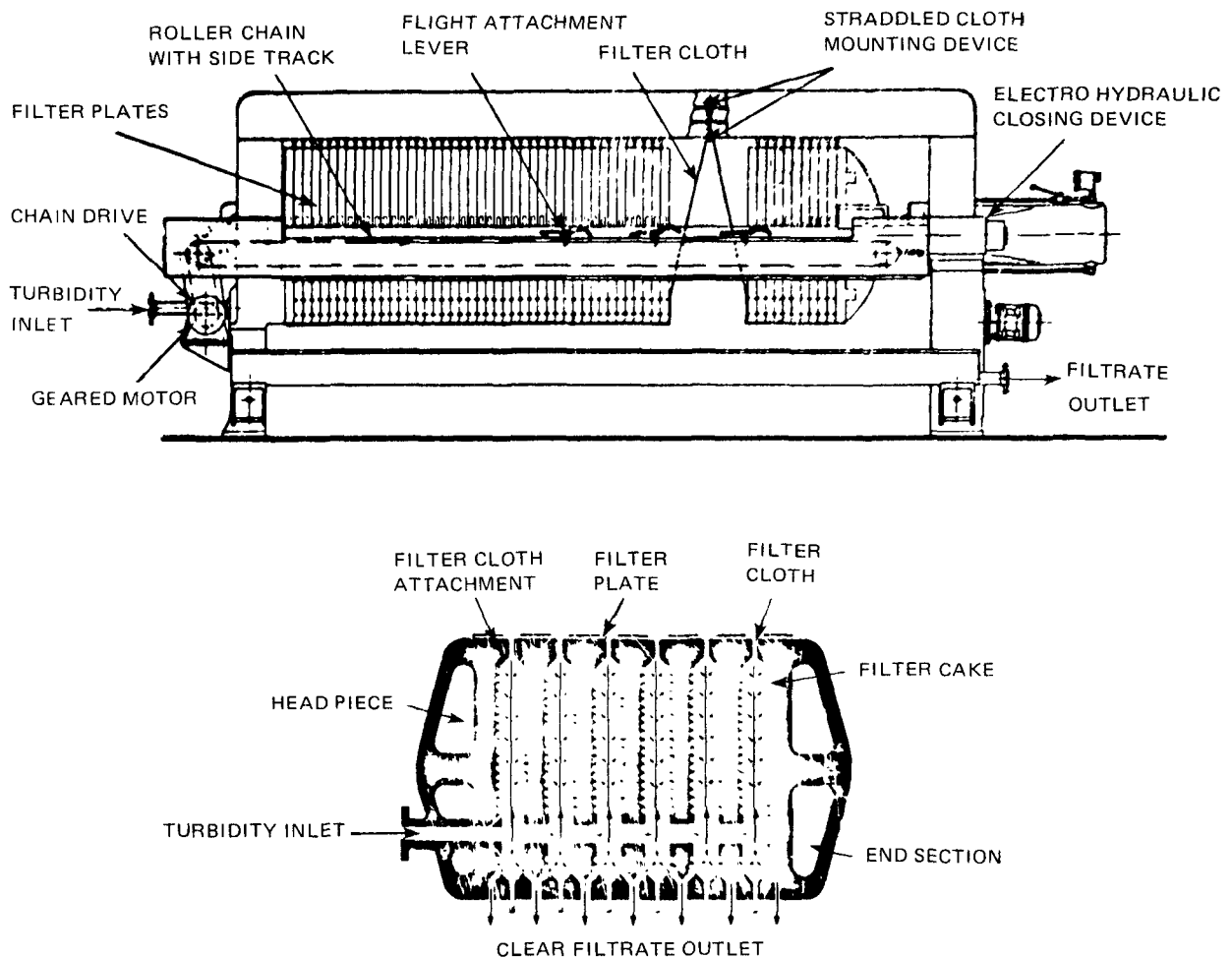

Figure IV-17. Chamber filter. (Courtesy of Eberhard Hoesch & Sohne.)
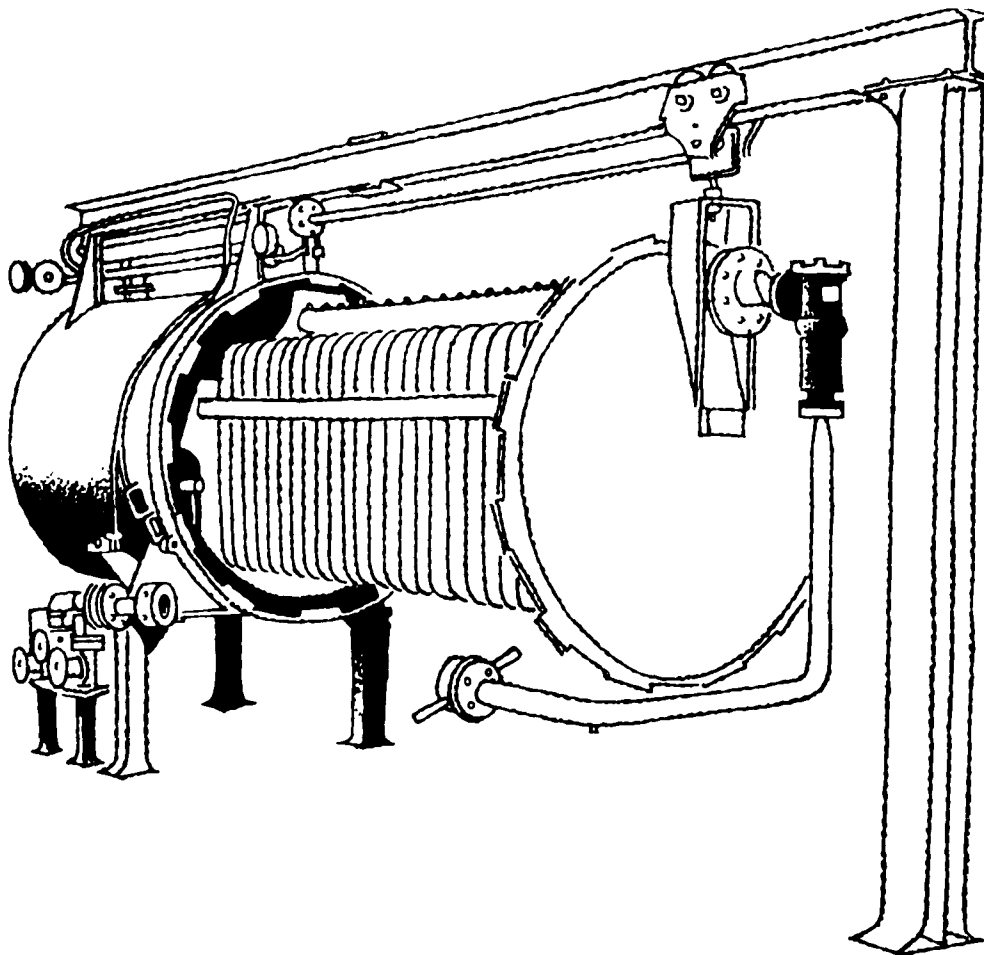
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Figure IV-18. Vertical leaf pressure filter, horizontal tank. (Courtesy of Johns-Manville Corporation.)

ULTIMATE DISPOSAL

For many years conventional disposal for metal-finishing sludges by the various industries operating waste-treatment systems was by dumping the thickened slurries or dry cakes on land areas prepared for receiving such wastes, with the aim of landfill soil buildup.

Today, with accelerated concern for the environment and for the safety of metal-waste solids disposal, the very best practices of some operations are just as much questioned as the injurious practices of others. It takes experience, discernment, and time to establish safe practices, and many local solid waste managers, under whose jurisdiction these concerns come, do not yet have either the experience or the accumulated knowledge to provide technical advice on the question of the suitability of disposal sites or disposal practices. The practice—of spreading the properly treated and inert metal-waste sludges on suitable ground area and periodically covering them to prepare a new deposit layer base—has worked without any known accident, ground contamination incident, or known harm. It must be acknowledged, of course, that the industries carrying on waste-treatment operations were few, and the consulting engineers advising them may have been well experienced. The aim usually was to find suitable ground area—possibly an abandoned quarry or excavation not suitable for any other purpose, or an area requiring fill to make it useful for future use. Spreading on land where growing vegetation may pick up toxic amounts of metal content should be carefully avoided.

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Properly treated metal-finishing waste solids are not soluble by rainwater washing; these metals, therefore, cannot infiltrate the ground and contaminate the ground water. This statement is true only if the sludges come from a well-operated treatment system. The common test to establish the suitability of a metal-finishing sludge for land disposal is the so-called leach test, which consists of stirring a preweighed amount of solid waste in distilled water and subsequently testing the water for significant constituents to establish the leachability of the waste. Distilled water has a far greater solubilizing effect than does the rainwater infiltrating the ground. Metals precipitated as hydroxides, carbonates, and trivalent chromium hydroxide are all sufficiently insoluble to indicate around 1 mg/l or less metal content in these leachate waters. An equally suitable and probably more economical test is to analyze the decant water over the sludge before filtration or discharge. If this filtrate is free of the metal constituents, chromic acid, cyanide, and so forth, the sludge may be considered safe for land disposal.

In general, sulfides should not be used for metal precipitation because the metal sulfides, in a manner similar to the typical sulfide commonly found in mine-waste residue, undergo bacterial decomposition, creating an acid condition if in contact with air and water. The acid so generated can redissolve the metal salts earlier precipitated.[32]

The greatest danger of ground contamination is from hexavalent chromium, which will infiltrate and can contaminate the aquifer if disposed on land. When ground water contamination occurs, it is not known how many years it will take until the chemicals are slowly leached out. It must be remembered that drinking water is considered unsafe for humans or animals if it contains more than 0.05 mg/l hexavalent chromium. It is evident from this example that the quantities of chromic acid that may cause significant ground contamination are very small. Another waste that must be carefully handled is precipitated calcium fluoride in solid form. Calcium fluoride has a residual solubility sufficiently high that it will continue to dissolve if washed by rainwater, and can infiltrate the ground, which may cause the fluoride content of the aquifer to exceed the established maximum limit of 1-1.5 mg/l allowed for drinking water. The best way to keep calcium fluoride solid discharges from infiltrating the ground is to prepare an impervious clay-layer disposal area and cover the waste with clay soil to provide the necessary foundation for subsequent calcium fluoride layers. Large quantities of calcium fluoride solids are, for instance, discharged by the video-tube-manufacturing and glass-working companies. Stainless steel processing also creates this type of solid waste problem.

Disposal of metal-finishing solid waste with garbage and other organic waste materials may cause limited resolubilization of the metal content, because the organic waste, as it undergoes anaerobic decomposition, releases organic acids which at pH 4.0-5.0 will have a limited solubilizing effect on the metal salts. While ground water contamination from these causes has not been observed, it is recommended that metal-waste solids be deposited in an area separate from that used for trash and other organic waste. To avoid the chance of an acid coming in contact with the metal salts and the subsequent leaching of metals, it is best to provide a first layer of limestone on which the metal solids are deposited. As the dump increases in size, some additional layers of limestone will aid the stabilization of the soil. The soil itself has good ion exchange capacity for metal salts, and this may be the reason that no investigations of the performance of the old metal-sludge lagoons and metal-disposal areas showed any evidence of potential injury to the water table.

The greatest danger lies in disposal of metal solids into the sanitary sewer systems, where they may accumulate with organic waste. As the digestion of the organic solids proceeds, the metal content in the organic residue constantly increases. The digested and stable organic wastes from the sanitary sewage treatment plant may be deposited on the land, as they are a most desirable fertilizer; but, at the same time, many of the metal salts, such as nickel, zinc, lead, and cadmium, are present in toxic quantities and may be taken up through the root system by growing vegetation.[33-39]

Incineration of metal waste, or of the sanitary organic solids mixed with metal waste, is also a potential and significant pollution danger. Zinc, lead, and cadmium will escape as gases into the

atmosphere, while trivalent chromium sludge will be reoxidized and will remain in the ashes as hexavalent chromium, with the usual solubility and contamination potential.[40]

Today many areas are faced with the problem of suitable disposal sites for the metal sludges from waste-processing operations. The best approach is to recognize that sludge disposal is a local problem that has to be solved by securing the cooperation of the regulatory agencies as close as possible to the locality where the treatment plant is operating. Some areas require the filtration of solids for maximum dryness. As this discussion shows, the required filtration adds to waste-treatment cost and is economical only for large plants where the savings in hauling costs will amortize the investment for the filter installation. The solid waste discharged on the land disposal site will not be distinguishable from the high-solids-content slurry after the first rain. Also, the slurry will dry to powdery consistency if the weather is dry. Solid waste disposal cannot be regulated as easily at the Federal level as at the local, even though general guidelines would be desirable. Under any circumstance, the decision regarding the land disposal site and its suitability will be a local question. It is hoped that the State regulatory agencies will offer guidance and advice for local decisionmaking bodies. In view of the recently significant portions of the metal-finishing wastes being treated, and the staggering volumes of sludges being created, it is only natural that there are problems of safe land disposal and of suitable disposal sites, and that they cannot be solved overnight.

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METRIC CONVERSION TABLES

Recommended Units

Description	Unit	Symbol	Comments	Customary Equivalents
Length	metre	m	*Basic SI unit*	39.37 in.=3.28 ft= 1.09 yd
	kilometre	km		0.62 mi
	millimetre	mm		0.03937 in.
	micrometre	μm.		$3.937 \times 10^{-3} = 10^3 A$
Area	square metre	m²		10.764 sq ft = 1.196 sq yd
	square kilometre	km²		6.384 sq mi = 247 acres
	square millimetre	mm²		0.00155 sq in.
	hectare	ha	The hectare (10 000 m²) is a recognized multiple unit and will remain in international use.	2.471 acres
Volume	cubic metre	m³		35.314 cu ft = 1.3079 cu yd
	litre	l	The litre is now recognized as the special name for the cubic decimetre.	1.057 qt = 0.264 gal = 0.81×10^{-4} acre-ft
Mass	kilogram	kg	*Basic SI unit*	2.205 lb
	gram	g		0.035 oz = 15.43 gr
	milligram	mg		0.01543 gr
	tonne or	t	1 tonne = 1 000 kg	0.984 ton (long) =
	megagram	Mg	1 Mg = 1 000 kg	1.1023 ton (short)
Time	second	s	*Basic SI unit*	
	day	d	Neither the day nor the year is an SI unit	
	year	year	but both are important.	
Force	newton	N	The newton is that force that produces an acceleration of 1 m/s² in a mass of 1 kg.	0.22481 lb (weight) = 7.233 poundals
Moment or torque	newton metre	N-m	The metre is measured perpendicular to the line of action of the force N. Not a joule.	0.7375 ft-lbf
Stress	pascal	Pa		0.02089 lbf/sq ft
	kilopascal	kPa		0.14465 lbf/sq in

Recommended Units

Description	Unit	Symbol	Comments	Customary Equivalents
Velocity linear	metre per second	m/s		3 28 fps
	millimetre per second	mm/s		0.00328 fps
	kilometres per second	km/s		2.230 mph
angular	radians per second	rad/s		
Flow (volumetric)	cubic metre per second	m³/s	Commonly called the cumec	15,850 gpm = 2.120 cfm
	litre per second	l/s		15.85 gpm
Viscosity	pascal second	Pa-s		0.00672 poundals/sq ft
Pressure	newton per square metre or pascal	N/m² / Pa		0.000145 lb/sq in
	kilometre per square metre or kilopascal	kN/m² / kPa		0.145 lb/sq in.
	bar	bar		14.5 b/sq in.
Temperature	Kelvin	K	*Basic SI unit*	$\frac{5F}{9} - 17.77$
	degree Celsius	C	The Kelvin and Celsius degrees are identical. The use of the Celsius scale is recommended as it is the former centigrade scale.	
Work, energy, quantity of heat	joule	J	1 joule = 1 N-m where metres are measured along the line of action of force N.	2.778×10^{-7} kw hr = 3.725×10^{-7} hp-hr = 0.73756 ft-lb = 9.48×10^{-4} Btu
	kilojoule	kJ		2.778 kw-hr
Power	watt	W	1 watt = 1 J/s	
	kilowatt	kW		
	joule per second	J/s		

Application of Units

Description	Unit	Symbol	Comments	Customary Equivalents
Precipitation, run-off, evaporation	millimetre	mm	For meteorological purposes it may be convenient to measure precipitation in terms of mass/unit area (kg/m³). 1 mm of rain = 1 kg/m²	
River flow	cubic metre per second	m³/s	Commonly called the cumec	35.314 cfs
Flow in pipes, conduits, channels, over weirs, pumping	cubic metre per second	m³/s		
	litre per second	l/s		15.85 gpm
Discharges or abstractions, yields	cubic metre per day	m³/d	1 l/s = 86.4 m³/d	1.83×10^{-3} gpm
	cubic metre per year	m³/year		
Usage of water	litre per person per day	l/person day		0.264 gcpd
Density	kilogram per cubic metre	kg/m³	The density of water under standard conditions is 1 800 kg/m³ or 1 000 g/l or 1 g/ml.	0.0624 lb/cu ft

Application of Units

Description	Unit	Symbol	Comments	Customary Equivalents
Concentration	milligram per litre	mg/t		1 ppm
BOD loading	kilogram per cubic metre per day	kg/m³d		0.0624 lb/cu-ft day
Hydraulic load per unit area; e.g. filtration rates	cubic metre per square metre per day	m³/m²d	If this is converted to a velocity, it should be expressed in mm/s (1 mm/s = 86.4 m³/m² day).	3.28 cu ft/sq ft
Hydraulic load per unit volume; e.g., biological filters, lagoons	cubic metre per cubic metre per day	m³/m³d		
Air supply	cubic metre or litre of free air per second	m³/s / l/s		
Pipes diameter	millimetre	mm		0.03937 in.
length	metre	m		39.37 in. = 3.28 ft
Optical units	lumen per square metre	lumen/m²		0.092 ft candle/sq ft

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